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Mathematics. — “*On the Motion of a Plane Fixed System with Two Degrees of Freedom*”. By Prof. W. VAN DER WOUDE. (Communicated by Prof. J. C. KLUYVER).

(Communicated at the meeting of January 30, 1926)

Literature.

I. FARID BOULAD: Sur la détermination du centre de courbure des trajectoires orthogonales d'une famille quelconque de courbes planes. (Bulletin des Sciences mathématiques, t. XL, 1916, p. 292—295).

II. G. DARBOUX: Remarque sur la note de M. FARID BOULAD. (Bulletin des Sciences mathématiques, t. XL, 1916, p. 295—296).

III. G. KOENIGS: Recherches sur les mouvements plans à deux paramètres. (Bulletin des Sciences mathématiques, t. XLI, 1917, pp. 120—127, 153—164, 181—196).

I. In the first of the above mentioned papers the author gives the theses which we reproduce here in a slightly altered form.

Let $[C]$ be an arbitrary system of curves, depending on one parameter; $[T]$ be the system of the orthogonal trajectories. Let a straight angle XOY move in such a way that the angular point O describes an arbitrary curve and OX and OY continually touch the curve (C) , resp. (T) , of the systems $[C]$ and $[T]$ which pass through O . In this case a plane system fixed to OXY has a motion with two degrees of freedom and any infinitesimal movement starting from an arbitrary initial position, defines a momentary pole of rotation I .

Now the theorems of FARID BOULAD read: “the locus of these poles I is a straight line d ; if in the considered position (C) and (T) are the two curves of which O is the intersection, d joins the centers of curvature of (C) and (T) . If further O describes a curve (Φ) which cuts the curves of $[C]$, hence also the curves of $[T]$, under a constant angle, — while, as we supposed, OX and OY continually touch curves of these systems —, I is at the same time the center of curvature of (Φ) ”.

II. In a note added to the above, the editor G. DARBOUX remarks that the first thesis of FARID BOULAD is a special case of the following one:

“If the motion of a figure in its plane depends on two parameters, to any infinitesimal movement of which the figure is capable, there

corresponds a definite pole of rotation; the locus of these poles is a straight line".

If the motion depends on the parameters u and v , it is easily seen — as DARBOUX remarks — that the projections of the displacement of a point (x, y) of the movable plane on axes fixed to this plane, are given by the expressions:

$$\begin{aligned} D_x &= (\xi_1 - \omega_1 y) du + (\xi_2 - \omega_2 y) dv \\ D_y &= (\eta_1 + \omega_1 x) du + (\eta_2 + \omega_2 x) dv \end{aligned} \quad \left. \vphantom{\begin{aligned} D_x \\ D_y \end{aligned}} \right\} 1)$$

in which the "translations" and "rotations" ξ, η, ω do not depend on the coordinates x and y .

A point which can be the center of rotation of any of these movements, must satisfy the condition

$$D_y = D_x = 0,$$

hence :

$$\begin{vmatrix} \xi_1 - \omega_1 y & \xi_2 - \omega_2 y \\ \eta_1 + \omega_1 x & \eta_2 + \omega_2 x \end{vmatrix} = 0$$

or

$$\xi_1 \eta_2 - \eta_1 \xi_2 + (\xi_1 \omega_2 - \xi_2 \omega_1) x + (\eta_1 \omega_2 - \eta_2 \omega_1) y = 0.$$

Consequently the locus of these points is a straight line.

III. The above mentioned papers have led G. KOENIGS to publish his investigations on "les mouvements plans à deux paramètres". It would take too much space if, however briefly, we reproduced these extensive considerations; it is the less necessary as we shall refer to him repeatedly. We therefore only draw the attention here to the remarkable thesis of KOENIGS which we mentioned in § 8.

Our aim is to derive the results of FARID BOULAD and KOENIGS, of the latter at least the main points, and a few more, in an entirely different way, so that for instance it becomes possible to treat entirely according to the general method the cases which require a special discussion of KOENIGS. Moreover we believe that the geometrical meaning of the used formulas appears more clearly in our method.

§ 1. Perhaps it is not quite unnecessary to draw the attention to the fact that by the movements with two degrees of freedom considered by DARBOUX and KOENIGS they always understand "holonomous" movements.

It would be easy to give examples which fall outside these. Let us assume for instance a straight angle with a system fixed to it which moves over a fixed plane; the path of the point O is entirely arbitrary whereas OX continually touches the path of O . Now O may coincide with any point A_1 of the fixed plane; but the position of OX does not only depend on A_1 but also on the path described by O .

1) These formulas will be derived in § 5.

We shall also exclude such non-holonomous movements; accordingly the position of the system of axes OXY is entirely defined by the point in the fixed plane which is reached by O .

§ 2. We begin by remarking that DARBOUX gives a proof of FARID BOULAD's starting point to which we have no objection, but that he undervalues the significance of this theorem; FARID BOULAD's theorem is as general as the one proved by DARBOUX.

Let Π_f be the fixed plane over which the plane Π_m moves to which the system of axes OXY is fixed; the position of Π_m or of OXY relative to a system of axes in Π_f depends on two parameters. We consider the line element (O, OX) of Π_m defined by the point O and the direction of the X -axis. If Π_m moves over Π_f , O will coincide with any point of Π_f and everywhere the line element (O, OX) will define a direction. In Π_f a singly infinite system of curves $[C]$ is defined in each point A_1 of which the tangent coincides with the direction defined in that point. Let $[T]$ be the system of the orthogonal trajectories. Now the movement of Π_m over Π_f is entirely defined by the condition that OX must continually coincide with the tangent to a curve of $[C]$, hence OY with the tangent to a curve of $[T]$. *Accordingly any plane movement with two degrees of freedom may be defined by fixing to the movable system a system of axes which moves in the way indicated by FARID BOULAD.*

§ 3. Now in the plane Π_f the systems of curves $[C]$ and $[T]$ are given; the movable system of axes has a definite position in which OX touches a curve (C) , OY a curve (T) .

We begin by accepting the proof given by DARBOUX of the first thesis of FARID BOULAD: the locus of the possible poles of rotation is a straight line d . These possible movements contain:

1. a displacement of O along (C) where OX continually touches (C) .
2. a displacement of O along (T) where OY continually touches (T) .

It is known that in the former case the pole of rotation coincides with the center of curvature of (C) , in the latter case with that of (T) . Consequently, as also FARID BOULAD and DARBOUX remark, the line d is the join of these points.

To this we shall add a few remarks. We have chosen OXY arbitrarily in the plane Π_m ; if we replace OXY by OX^1Y^1 where $\angle XOX^1 = \varphi$, also the line element (O, OX^1) describes the whole plane Π_f ; in the possible movements, the system of curves $[C]$ is replaced by another system $[C^1]$, formed by isogonal trajectories (φ -trajectories) of $[C]$.

Whereas accordingly the two-dimensional system of possible movements which in the future we shall indicate by M_2 , is quite defined by the system of curves $[C]$, the reverse, that M_2 quite defines this system of curves, is not true. If we replace $[C]$ by $[C^1]$, M_2 does not change;

but then d , the locus of the poles of rotation for an arbitrary position, has not changed either.

Consequently any point I of d is not only a possible pole of rotation, but also the center of curvature of one of the isogonal trajectories of (C) in O .

This is the last thesis of FARID BOULAD. We may also formulate its geometrical contents in the following way:

The centers of curvature of (C) and (T) form with O the angular points of a right-angled triangle; the hypotenuse also contains the center of curvature of (C^1) . If R_1, R_2, R_φ are the radii of curvature of these three curves in O , we have:

$$\frac{1}{R_\varphi} = \frac{\cos \varphi}{R_1} + \frac{\sin \varphi}{R_2} \quad (1)$$

$(0, R_1)$ and $(-R_2, 0)$ are the centers of curvature of (C) and (T) .

§ 4. This gives us at once the solution to the problem: to produce two mutually orthogonal systems of curves so that the ratio of the radii of curvature of two curves which cut each other in a given point, is constant, i.e. independent from the chosen point.

Let m be this constant and $\cotg \varphi = m$. We consider an arbitrary singly-infinite system of straight lines together with the systems of their orthogonal trajectories $-\varphi$ - and $(\frac{1}{2}\pi + \varphi)$ -trajectories. In any point the following relations between the radii of curvature exist:

$$\frac{1}{R_\varphi} = \frac{\sin \varphi}{R_{1/2\pi}}; \quad \frac{1}{R_{(1/2\pi + \varphi)}} = \frac{\cos \varphi}{R_{1/2\pi}};$$

$$\frac{R_\varphi}{R_{(1/2\pi + \varphi)}} = \cotg \varphi = m.$$

Accordingly the φ - and the $(\frac{1}{2}\pi + \varphi)$ -trajectories give the solution of the problem.

§ 5. We shall now give a geometrical meaning to the quantities which appear in the note of DARBOUX.

If on an arbitrary surface we choose orthogonal parameter curves $v = \text{constant}$ and $u = \text{constant}$, and if we make a system of axes $OXYZ$ move in such a way that O describes this surface, OX and OY touch the u - and v -curves and OZ coincides with the normal to the surface,

¹⁾ Cf. the more general theorem (LIOUVILLE, 1850): if on a surface ρ_u and ρ_v are the geodetical curvatures of the orthogonal systems of curves u and v , we have for a curve which cuts the curves of the u -system (i.e. $v = \text{constant}$) under an angle φ :

$$\frac{1}{\rho_g} = \frac{d\varphi}{ds} + \frac{\cos \varphi}{\rho_u} + \frac{\sin \varphi}{\rho_v}.$$

the movements of the trihedron $OXYZ$, hence also the infinitesimal displacement of a point (x, y, z) fixed to this trihedron, may be expressed by geometrical quantities that are related to the parameter curves. (By the u -curves we always understand the curves $v = \text{constant}$).

If the parameter curves are at the same time lines of curvature, these expressions assume a more simple form.

Let us apply this by assuming the systems $[C]$ and $[T]$ as u - and v -curves; they may be considered as lines of curvature of Π_f . In this case the possible infinitesimal displacements of a point (x, y) are expressed by ¹⁾:

$$\left. \begin{aligned} D_x &= \sqrt{E} \left(1 - \frac{y}{R_1} \right) du - \sqrt{G} \frac{y}{R_2} dv \\ D_y &= \sqrt{E} \frac{x}{R_1} du + \sqrt{G} \left(1 + \frac{x}{R_2} \right) dv \end{aligned} \right\} \dots \dots \dots (2)$$

Here du and dv are the increments of the coordinates of the point O in the plane Π_f , D_x and D_y are the projections of the infinitesimal displacement of a point (x, y) on OX and OY ; (o, R_1) is the center of curvature of the u -curve ($v = \text{constant}$), $(-R_2, o)$ that of the v -curve in the point O ²⁾, E and G are the values which the coefficients in the expression for the line element of:

$$ds^2 = Edu^2 + Gdv^2$$

assume in the point O .

We remark that between E and G there exists a relation, the formula of GAUSZ, which indicates that the total curvature of Π_f is zero:

$$\frac{\partial}{\partial u} \left(\frac{1}{\sqrt{E}} \frac{\partial \sqrt{G}}{\partial u} \right) + \frac{\partial}{\partial v} \left(\frac{1}{\sqrt{G}} \frac{\partial \sqrt{E}}{\partial v} \right) = 0; \dots \dots \dots (3)$$

further that R_1 and R_2 are expressed in E and G by

$$\frac{1}{R_1} = -\frac{1}{\sqrt{EG}} \frac{\partial \sqrt{E}}{\partial v}; \quad \frac{1}{R_2} = \frac{1}{\sqrt{EG}} \frac{\partial \sqrt{G}}{\partial u} \dots \dots \dots (4)$$

This enables us to write the formula of GAUSZ in the following form, which will appear to be more suitable for us:

$$\sqrt{G} \frac{\partial}{\partial u} \frac{1}{R_2} - \sqrt{E} \frac{\partial}{\partial v} \frac{1}{R_1} + \sqrt{EG} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) = 0 \dots \dots (3^a)$$

From (2) we find as the equation of the line d , the locus of the poles of rotation:

¹⁾ G. DARBOUX: *Théorie des Surfaces*, t. II, p. 398; GAUTHIER-VILLARS, Paris; 1915.

²⁾ R_2 may therefore differ in sign from the radius of curvature of $u = \text{constant}$, if we wish to consider this radius of curvature as a positive quantity.

§ 9. If a point $P(x, y)$, that is a point with coordinates (x, y) relative to OXY , is *fixed* — i.e. if it is at rest relative to Π_f —, these coordinates satisfy the conditions:

$$\left. \begin{aligned} V_{a,x} &\equiv \xi - \omega y + \frac{dx}{dt} = 0 \\ V_{x,y} &\equiv \eta + \omega x + \frac{dy}{dt} = 0 \end{aligned} \right\} \dots \dots \dots (9)$$

Here, as always, ξ and η are the velocity-components of O and ω is the rotation of the system of axes OXY .

If the line (8) is to be at rest relative to Π_f , there must be an infinite number of pairs of values x and y which satisfy (8) and (9), hence also the equation which is found from (8) through differentiation:

$$x \frac{da}{dt} + y \frac{d\beta}{dt} + a \frac{dx}{dt} + \beta \frac{dy}{dt} = 0 \dots \dots \dots (10)$$

By eliminating $\frac{dx}{dt}$ and $\frac{dy}{dt}$ out of this equation and (9), we find:

$$\left(\frac{da}{dt} - \beta\omega \right) x + \left(\frac{d\beta}{dt} + a\omega \right) y - a\xi - \beta\eta = 0 \dots \dots (11)$$

Now an infinite number of values x and y must satisfy (8) and (11); for this it is necessary and sufficient that:

$$\left\| \begin{array}{ccc} a & \beta & 1 \\ \frac{da}{dt} - \beta\omega & \frac{d\beta}{dt} + a\omega & a\xi + \beta\eta \end{array} \right\| = 0 \dots (12)$$

This expresses the conditions in question.

We shall now return to the considered system M_2 ; we choose a movement out of it which depends on one parameter, by considering v as a function of u . If we put:

$$\frac{dv}{du} = \lambda,$$

the conditions that in this movement the line

$$\frac{x}{-R_2} + \frac{y}{R_1} - 1 = 0$$

is at rest relative to Π_f , are expressed by (12) on condition that we apply the following substitutions:

$$\left. \begin{aligned} a &= -\frac{1}{R_2} \quad , \quad \beta = \frac{1}{R_1} \\ \xi &= \sqrt{E} \quad , \quad \eta = \lambda \sqrt{G} \quad , \quad \omega = \frac{\sqrt{E}}{R_1} + \lambda \frac{\sqrt{G}}{R_2} \\ \frac{d}{dt} &= \frac{\partial}{\partial u} + \lambda \frac{\partial}{\partial v} \end{aligned} \right\} \dots (13)$$

The conditions found above assume the following form:

$$\left. \begin{aligned} \frac{\partial}{\partial u} \frac{1}{R_2} + \lambda \frac{\partial}{\partial v} \frac{1}{R_2} + \sqrt{E} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) &= 0 \\ \frac{\partial}{\partial u} \frac{1}{R_1} + \lambda \frac{\partial}{\partial v} \frac{1}{R_1} - \lambda \sqrt{G} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) &= 0 \end{aligned} \right\}$$

By means of (3^a) they may be reduced to

$$\left. \begin{aligned} \lambda \sqrt{G} \frac{\partial}{\partial v} \frac{1}{R_2} + \sqrt{E} \frac{\partial}{\partial v} \frac{1}{R_1} &= 0 \\ \lambda \sqrt{G} \frac{\partial}{\partial u} \frac{1}{R_2} + \sqrt{E} \frac{\partial}{\partial u} \frac{1}{R_1} &= 0 \end{aligned} \right\} \dots \dots \dots (14)$$

If always the same value of λ is to satisfy them, in other words if in any position the system M_2 is to contain a movement which lets d be at rest in Π_f , it is necessary and sufficient that:

$$\left| \begin{array}{cc} \frac{\partial}{\partial u} \frac{1}{R_1} & \frac{\partial}{\partial v} \frac{1}{R_1} \\ \frac{\partial}{\partial u} \frac{1}{R_2} & \frac{\partial}{\partial v} \frac{1}{R_2} \end{array} \right| = 0 \dots \dots \dots (15)$$

As we found above the condition which must be satisfied if M_2 is always to contain a movement in which d does not move in Π_m , is

$$\varphi(R_1, R_2) = 0 \dots \dots \dots (16)$$

But the two conditions (15) and (16) have the same meaning. The first part of the theorem of KOENIGS is therefore proved.

The movement where d is at rest in Π_m , is given by:

$$\frac{1}{R_1} = \text{constant},$$

or

$$\frac{\partial}{\partial u} \frac{1}{R_1} du + \frac{\partial}{\partial v} \frac{1}{R_1} dv = 0;$$

the movement which lets d be at rest in Π_f , is expressed by (cf. 14):

$$\sqrt{E} \frac{\partial}{\partial u} \frac{1}{R_1} du + \sqrt{G} \frac{\partial}{\partial u} \frac{1}{R_2} dv = 0.$$

These two movements are the same as:

$$\sqrt{E} \frac{\partial}{\partial v} \frac{1}{R_1} - \sqrt{G} \frac{\partial}{\partial u} \frac{1}{R_2} = 0,$$

or as (cf. 3^a):

$$\sqrt{EG} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) = 0.$$

If we restrict ourselves to real movements, this is only the case if $\frac{1}{R_1} = \frac{1}{R_2} = 0$.

Only if all the movements are translations, the displacements for which d is at rest in Π_m coincide with those for which d is at rest in Π_f ; except in this trivial case they are independent from each other.

In this way also the second part of the theorem in question has been proved.

The only point which is left is to draw the attention to the elegant construction of KOENIGS for these systems M_2 in which the motion of d depends on one parameter. Choose a curve ζ_f in Π_f and a curve ζ_m in Π_m both of which touch d ; let alternately d roll over ζ_f and ζ_m over d ; the system M_2 is linearly composed of these displacements.

§ 10. We shall return a moment to the quantities of the second order which appear in the movements of a system M_2 , which we now again assume arbitrary.

In an initial position chosen at random O has again a definite situation in Π_f , OX touches the u -curve through that point; the tangent to the path described by an arbitrary point of Π_m , only depends on the ratio of du and dv , the increments of the coordinates of O . We can begin by making O describe different paths which all have the same tangent in the initial position; now the corresponding paths of the other points of Π_m also have the same tangents in the initial position but different curvatures.

In the future we shall only consider infinitesimal displacements for which

$$\frac{dv}{du} = \lambda$$

has a given value, whereas

$$\frac{d^2v}{du^2} = \lambda'$$

may assume any value. The pole of rotation I is always the same point.

§ 11. In the movement of a plane fixed system Π_m of which the position is defined by one parameter, which for the sake of more convenient expression we shall for the moment identify with time and indicate by t , the quantities of the first order are defined by the pole of rotation I , those of the second order by a point K^1 , the other extreme of the diameter of the inflectional circle through I .

For the velocity- and acceleration-components of a point fixed to Π_m , we have resp.

$$\left. \begin{aligned} V_x &= \xi - \omega y \\ V_y &= \eta + \omega x \end{aligned} \right\}$$

and

$$\left. \begin{aligned} J_x &= \frac{d\xi}{dt} - \omega\eta - \frac{d\omega}{dt}y - \omega^2x \\ J_y &= \frac{d\eta}{dt} + \omega\xi + \frac{d\omega}{dt}x - \omega^2y \end{aligned} \right\}^1)$$

The equation of the inflectional circle is in this case

$$\begin{vmatrix} V_x & V_y \\ J_x & J_y \end{vmatrix} = 0$$

or

$$\omega^3(x^2 + y^2) + \left(\frac{d\omega}{dt}\xi - \frac{d\xi}{dt}\omega + 2\omega^2\eta\right)x + \left(\frac{d\omega}{dt}\eta - \omega\frac{d\eta}{dt} - 2\omega^2\xi\right)y + \dots = 0.$$

This gives us at once the center of the inflectional circle and at the same time the point K^1 , as $I\left(-\frac{\eta}{\omega}, \frac{\xi}{\omega}\right)$ is also known.

We find

$$x_{K^1} = \frac{-\frac{d\omega}{dt}\xi + \frac{d\xi}{dt}\omega - \omega^2\eta}{\omega^3} ; \quad y_{K^1} = \frac{-\frac{d\omega}{dt}\eta + \frac{d\eta}{dt}\omega - \omega^2\xi}{\omega^3}.$$

If we return to the case under consideration we must make the following substitutions:

$$\begin{aligned} \xi &= \sqrt{E}; \quad \eta = \lambda\sqrt{G}; \quad \omega = \frac{\sqrt{E}}{R_1} + \lambda\frac{\sqrt{G}}{R_2} \\ \frac{d}{dt} &= \frac{\partial}{\partial u} + \lambda\frac{\partial}{\partial v}. \end{aligned}$$

Then we must consider λ as a constant, λ' as a parameter. In this way we find the locus of K^1 represented by

$$\begin{aligned} \left(\frac{\sqrt{E}}{R_1} + \lambda\frac{\sqrt{G}}{R_2}\right)^3 x &= -E\frac{d}{du}\frac{1}{R_1} - \lambda\sqrt{EG}\frac{d}{du}\frac{1}{R_2} - \lambda\frac{\sqrt{E}}{R_2}\frac{d\sqrt{G}}{du} + \\ &\quad + \lambda\frac{\sqrt{G}}{R_2}\frac{d\sqrt{E}}{du} + \lambda'\frac{\sqrt{EG}}{R_2} \\ \left(\frac{\sqrt{E}}{R_1} + \lambda\frac{\sqrt{G}}{R_2}\right)^3 y &= -\lambda\sqrt{EG}\frac{d}{du}\frac{1}{R_1} - \lambda^2 G\frac{d}{du}\frac{1}{R_2} + \lambda\frac{\sqrt{E}}{R_1}\frac{d\sqrt{E}}{du} - \\ &\quad - \lambda\frac{\sqrt{G}}{R_1}\frac{d\sqrt{E}}{du} + \lambda'\frac{\sqrt{EG}}{R_1} \\ &\quad \left(\text{where } \frac{d}{du} = \frac{\partial}{\partial u} + \lambda\frac{\partial}{\partial v}\right). \end{aligned}$$

¹⁾ G. KOENIGS: Leçons de Cinématique; p. 142; A. HERMANN, Paris; 1897.

If we eliminate λ' the equation of this locus is

$$\left(\frac{\sqrt{E}}{R_1} + \frac{\sqrt{G}}{R_2}\right)^2 \left(\frac{x}{R_1} + \frac{y}{R_2}\right) + \sqrt{E} \frac{d}{du} \frac{1}{R_1} + \sqrt{G} \frac{d}{du} \frac{1}{R_2} = 0.$$

This represents a line h perpendicular to d ; its intersection with d we call H .

§ 12. If now we consider λ as a variable, I and H move along d ; the correspondence between I and H has been elaborately treated by KOENIGS. We shall not enter into it but we shall only point out the following properties.

Again we suppose λ to be a constant; I and H are fixed points of d and h is the locus of K^1 . As IK^1 is always a diameter of the inflectional circle we have:

for all the displacements with the same pole of rotation the inflectional circles form a pencil with I and H as base points; in each of these displacements H describes a point of inflection in which the tangent coincides with h .

For each of these displacements on d the pole of rotation as well as the point of intersection with the inflectional circle are fixed; hence:

In all these displacements all points of d have the same radius of curvature.

Mathematics. — "A Representation of the Bisecants of a Rational Twisted Curve on a Field of Points." By Prof. JAN DE VRIES.

(Communicated at the meeting of February 27, 1926)

1. The points A of a rational twisted curve α^n may be brought into a projective correspondence with the points C of a conic γ^2 . If C_1 and C_2 correspond to A_1 and A_2 and if B is the point of intersection of the lines c_1 and c_2 which touch γ^2 at C_1 and C_2 , B may be considered as the *image* of the bisecant b which joins A_1 to A_2 .

Now the point range (B) on c_1 is the image of the cone $(b)^{n-1}$ which projects α^n out of A_1 and C_1 is the image of the *tangent* at A_1 .

The scroll of the bisecants which rest on a line l , has $(n-1)$ bisecants in common with the cone $(b)^{n-1}$; hence its image cuts the tangent c in $(n-1)$ points B and is a curve λ^{n-1} .

The curves λ^{n-1} and μ^{n-1} have $(n-1)^2$ points in common; accordingly on the lines l and m there rest $(n-1)^2$ bisecants and the scroll which is represented on λ^{n-1} , is of the degree $(n-1)^2$. As, evidently, a plane through l contains $\frac{1}{2}n(n-1)$ chords, l is a multiple directrix of which any point carries $\frac{1}{2}(n-1)(n-2)$ chords.

If l cuts the curve α^n in A , the said scroll consists of the cone $(b)^{n-1}$, that has A as vertex, and a scroll of the degree $(n-1)(n-2)$, etc.

2. We shall now consider the case $n=4$ more closely.

To l as directrix of bisecants b of an α^4 there corresponds a scroll Δ^9 represented on a λ^3 . As λ^3 contains six points of γ^2 , the *tangents* to α^4 form a scroll of the sixth order.

The curves λ^3 form a system ∞^4 . Through four points B_k chosen at random there pass *two* curves, for the corresponding bisecants b_k have two transversals l .

To a secant s with point of intersection A there corresponds the system of a scroll Σ^6 and the cone $(b)^3$. Now the curve λ^3 consists of a conic σ^2 and a tangent c to γ^2 . The curves σ^2 form a system ∞^3 .

The hyperboloid through three bisecants has 2 more points in common with α^4 ; through each of these points there passes a secant s , which rests on the three lines b . Consequently three points B generally define two conics σ^2 .

The chords b_1, b_2 , which are represented in B_1, B_2 , are cut by one chord d . For b_2 cuts the scroll Δ_1^3 corresponding to b_1 in one point outside α^4 and through this point there passes one generatrix of Δ_1^3 , which is a chord resting on b_1 and b_2 . Hence *any* straight line δ represents a scroll Δ^3 .

3. For a trisecant t the scroll \mathcal{A}^9 consists of three cones which have the points of intersection A_k of t with α^4 as vertices.

The line t is represented in the angular points B_k of a triangle circumscribed about γ^2 . As each point of α^4 carries only one trisecant, the corresponding points C_k on γ^2 form a cubic involution and the same is the case with the tangents c_k . Accordingly the trisecants are represented on a conic β^2 , the "*involution curve*" of the second cubic involution.

The points of intersection of β^2 with a curve λ^3 form two triplets of the cubic involution of the image points B_k . Hence two trisecants rest on l and the lines t form a *quadratic scroll*.

The points of intersection of β^2 and γ^3 are the images of four trisecants which touch α^4 .

Any conic σ^2 is an *involution curve*; for the planes through a secant s define a cubic involution on α^4 , so that the images B of the chords in one of these planes form a group of an I^3 on σ^2 . Evidently the conic β^2 belongs to the system of the σ^2 ; but it belongs to ∞^1 secants (these form the second scroll of the hyperboloid of the trisecants).

Also the curves λ^3 are involution curves, for any plane through l contains six chords and these are represented in the angular points of a quadrangle circumscribed about γ^2 .

4. Through any point of the chord d there pass two chords b_1, b_2 ; the planes b_1b_2 pass through the single directrix e of Δ^3 .

The pairs of points B_1, B_2 form an involution I^2 on the image line δ ; its double points are the images of the torsal lines k of Δ^3 . These are bisecants which join the points of contacts of two intersecting tangents and which, therefore, lie in a double tangent plane to α^4 . Hence the directrix e is the intersection of two double tangent planes.

To any line e there corresponds a definite bisecant d ; it rests on the *tangent chords* k of the two double tangent planes.

For a bisecant k Δ^3 is a scroll of CAYLEY; for in this case k is a directrix and at the same time a generatrix, hence a directrix e .

5. The image δ of a Δ^3 contains the images K of two chords k ; consequently the system of the tangent chords is represented on a conic k^2 . As this has six points in common with a λ^3 , the *tangent chords* form a scroll of the *sixth* degree.

To the image δ of a Δ^3 there corresponds the image D of the chord d on which the bisecants b of Δ^3 rest. Evidently D and δ correspond to each other in a polar correspondence. The image K of a chord k lies on the line δ^* corresponding to k ; hence D and δ are polar relative to the conic k^2 and two points D_1 and D_2 harmonically separated by k^2 , are the images of two intersecting bisecants.

A polar triangle corresponds to three bisecants which come together in a point outside α^4 .

6. Two point triplets chosen at random on α^4 , define a cubic involution I^3 . Any group of the I^3 defines three straight lines b of a scroll

(b), the *involution scroll*. This is represented on an involution conic $(B)^2$ of γ^2 . The conics $(B)^2$ form a system ∞^4 ; the bisecants which are represented in four arbitrary points B_k , define two I^3 on α^4 ; accordingly through four points there pass *two* conics $(B)^2$.

$(B)^2$ has six points in common with a λ^3 ; hence the involution scroll is a $(b)^6$.

Through the angular points of a triangle circumscribed about γ^2 and two arbitrary points B , there passes only one $(B)^2$; for an I^3 is quite defined by a triplet and two pairs.

Two triangles circumscribed about γ^2 also define only one $(B)^2$, hence one I^3 on α^4 .

7. The involution scroll of an I^4 is represented on a curve $(B)^3$ which is circumscribed about ∞^1 quadrangles formed by tangents to γ^2 . As $(B)^3$ has nine points in common with λ^3 the scroll (b) has the degree 9.

As two groups of the I^4 are equivalent to 6 pairs, the curves $(B)^3$ form a system ∞^6 . Through the angular points of two quadrangles circumscribed about γ^2 , there passes one $(B)^3$; also through the angular points of three arbitrary triangles circumscribed about γ^2 .

8. Let φ^2 be an arbitrary conic in the image plane. The tangents c through its points to γ^2 define on this curve an involutory correspondence (2,2), hence also a (2,2) between the points of α^4 . The bisecants through associated points form a scroll $(b)^6$, for φ^2 has six points in common with a curve λ^3 .

An involutory (2,2) is defined by 5 pairs; consequently the conics φ^2 form a system ∞^5 .

The bisecants resting on a conic ε^2 through four points E_k of α define a (2,2) on α^4 . For the cone $(b)^3$ which has a point A of α^4 as vertex, cuts ε^2 outside E_k in two more points and therefore contains two chords which rest on ε^2 .

The scroll $(b)^6$ of the bisecants resting on ε^2 , has α^4 as double curve and ε^2 as triple curve.

Chemistry. — "*The use of Salicylic acid as a standard in Calorimetry.*"
By ERNST COHEN, P. E. VERKADE, SABURO MIYAKE, J. COOPS Jr.,
and J. A. VAN DER HOEVE.

(Communicated at the meeting of January 30, 1926).

Introductory.

The investigations of recent years had led to the conviction that, when determining the heats of combustion of substances, the first desideratum is to ascertain with great accuracy the heats of combustion of one or more "standard-substances", and since that time similar studies have been taken up by more than one scientist ¹⁾. Contrary to the opinion of some investigators VERKADE and COOPS have pointed out that not only of one standard-substance the heat of combustion ought to be fixed with great accuracy, but at least of two of such substances.

As the result of an extensive investigation they have recommended *salicylic acid* as second standard with *benzoic acid* as first standard ²⁾.

As ERNST COHEN and VAN DOBBENBURCH ³⁾ had found that this acid, when recrystallized, without further precautions, from water, can contain rather considerable quantities of occluded water, which cannot be removed by drying in vacuo over P_2O_5 , the question arose if the few considerations mentioned by VERKADE and COOPS in their paper just cited, relating to the previous history of the preparates they had investigated, could be considered sufficient to guarantee a *salicylic acid* preparate which was perfectly free from water. For, at that time, a complete formula for the preparation of a standard-preparate, had not yet been given.

While later on we shall return in extenso to this subject, we give here the results of our investigation in this direction; it has proved that, indeed, the determination of the heat of combustion of *salicylic acid* which has been recrystallized from water, without further precautionary measures, can give quite arbitrary values. However, we can add the assurance that *if, after recrystallizing from water, the acid is crystallized from dry ether, we always find the same value for the heat of combustion, viz. the one which VERKADE and COOPS have fixed for it.*

¹⁾ See for literature f. i. P. E. VERKADE, *Chemisch Weekblad* 21, 13 (1924).

²⁾ *Rec. d. Trav. Chim. des Pays Bas* 43, 561 (1924).

³⁾ *These Proceedings* 28, 702, (1925).

The Method of Procedure.

§ 1. The different preparates under discussion have been prepared at Utrecht or at Rotterdam, at which latter place the calorimetric measurements were made in the Laboratory of the Handels-Hoogeschool, with the apparatus used by VERKADE and COOPS in their previous investigations. The preparates which were got ready at Utrecht were taken to Rotterdam sealed in glass bottles, which had been well dried. When the calorimetric determinations had been made we transported the rest of the preparations used to Utrecht in the same way, and here we determined ¹⁾, if necessary, the solubility in dry benzene at 30°.00 C. This was done after the manner minutely described in the paper by ERNST COHEN and VAN DOBBENBURGH ²⁾. In the course of this paper we shall indicate this communication by the letters V. C. D.

The solubility determinations have all been made by SABURO MIYAKE. The names behind the preparates indicate their maker.

The preparates used.

§ 2. The preparates of salicylic acid which were calorimetrically investigated were :

A. Standard preparete (MIYAKE). A newly received quantity of salicylic acid (KAHLBAUM, für kalorimetrische Bestimmungen) was recrystallized (V.C.D § 2, 2), from dry ether (V.C.D. § 1, c), kept for some weeks over P_2O_5 in vacuo, and powdered every day.

B. Ether preparete I (v. D. HOEVE). Prepared in quite the same way as A. On the 9th of October the air-dry preparete was placed in vacuo over P_2O_5 , and, in flat weighing bottles, in which a thin layer of acid (± 7 gms) had been spread, the weight was occasionally determined. Before weighing the preparete into the bottles it had been powdered a few times. Thus we found: October 12: 43.9791; October 19: 43.9789; October 20: 43.9789; October 21: 43.9790 gms.

C. Ether preparete 2 (v. D. HOEVE). Quite as B. Placed in vacuo (± 5 gms. of acid) on October 11. Found: October 16: 39.7814; October 19: 39.7810; October 20: 39.7809; October 21: 39.7812; October 22: 39.7814 gms.

D. Water preparete I (v. D. HOEVE). The acid had been slowly crystallized from the aqueous solution. After sucking off on a hardened filter the crystals were left on a glass plate to become air-dry. When the mass had been in vacuo for some time, it was powdered and for 72 hours placed in vacuo over P_2O_5 . When the weight had become constant a part was kept as "Water preparete I" (± 10 gms. of acid). Found October

¹⁾ Not at 30°.50 C., as was previously done by COHEN and VAN DOBBENBURGH.

²⁾ These Proceedings 28, 702, (1925).

23 : 44.4869 gms. ; October 24 : 44.4867 gms. ; October 26 : 44.4866 gms., while the rest was powdered a few times, and then also dried to constant weight in vacuo over P_2O_5 (± 10 gms. of acid). Found : October 26 : 43.4416 gms. ; October 28 : 43.4366 gms. ; October 29 : 43.4363 gms. ; October 30 : 43.4363 gms.

E. Water preparete II is this last mentioned part. (V. D. HOEVE).

F. Water preparete, chilled on ice, (V. D. HOEVE). Pure ice was washed with distilled water ; on 1 K.G. of ice was poured a boiling saturated aqueous solution of about 30 gms. of salicylic acid. The crystals were sucked off and made air-dry. Then it was placed in vacuo, 48 hours later it was powdered, and dried in the desiccator to constant weight.

G. Water preparete. After continual powdering we allowed preparete E to stand for a week in vacuo over P_2O_5 ; the preparete thus treated is called G.

Moreover we have investigated :

H. Preparete "KAHLBAUM für kalorimetrische Bestimmungen" (new consignment), coarse crystalline, was, without further treatment, powdered and kept over P_2O_5 in vacuo for 288 hours.

I. Preparete POULENC ("Standard pour calorimétrie"). On November 12 this preparete was quickly recrystallized from water, stirring the solution continuously (VERKADE). After sucking off and washing with water it was placed in vacuo over P_2O_5 without first powdering it. The heat of combustion was determined on November 14, 17 and 24.

K. Preparete I, without special preliminary treatment, was heated for 6 hours at 100° — 105° (VERKADE).

L. Another part of preparete I was powdered and then heated for six hours at 100° — 105° (VERKADE).

The results.

§ 3. The results of the determinations of the heat of combustion of the different preparates are given in Table 1. Before the combustion every preparete was always carefully made homogeneous.

When the preparates had been transported to Utrecht their solubility was determined in dry benzene (MIYAKE). The benzene had been treated in the same way as previously described (V.C.D. § 1. b.). The solubilities thus found are also given in Table 1.

§ 4. First of all we wish to point out that the heat of combustion of the preparates A, B, and C, all recrystallized from dry ether, is exactly the same as the one found by VERKADE and COOPS for preparates of very different origin, viz. 5242 cal.₁₅₀ per gramme (air).

The satisfactory agreement between the values which we found in the different determinations of each of these preparates indicates that they were homogeneous. The fact that the solubility determinations for different samples in dry benzene give concurring figures is in correspondence with it.

TABLE 1.

Name of the preparate	Heat of combustion in cal. 15° per gram (air)	Solubility at 30°.0 C. in dry benzene gms in 100 gms, of saturated solution	
		First determination	Second determination
<i>A</i>	5243.1 } 5242.3 } 5243.4 5244.7 }	0.98 ²	0.98 ²
<i>B</i>	5242.4 } 5244.5 } 5243.4	0.98 ²	0.97 ⁵
<i>C</i>	5239.9 } 5243.6 } 5241.7	0.97 ⁹	0.98 ²
<i>D</i>	5232.8 } 5232.6 } 5233.8 5237.3 } 5232.4 }	0.98 ⁵	1.00 ⁰
<i>E</i>	5237.4 } 5229.7 } 5231.8 5230.0 } 5229.4 }	0.99 ²	0.97 ⁷
<i>F</i>	Nov. 3-4 5219.7 } 5223.3 } 5216.3 } Nov. 14 5240.8 } 5228.7 5240.8 } 5228.0 } 5232.0 }	1.00 ¹	1.00 ⁸
<i>G</i>	5235.6 } 5232.1 } 5236.2 5235.1 } 5242.0 }	—	—
<i>H</i>	5243.1 } 5242.5 } 5242.4 5244.4 } 5239.6 }	—	—
<i>I</i>	5222.1 } 5216.8 } 5220.3 5221.9 }	—	—
<i>K</i>	5231.4 } 5233.8 } 5232.6	—	—
<i>L</i>	5237.8 } 5238.0 } 5237.9	—	—

§ 5. The course is totally different with the preparates D, E, F and I, all of which are crystallized from water. Without exception they give for the heat of combustion values which are far too low. Moreover the figures obtained from one and the same preparete in different experiments are often greatly divergent, which proves that the samples taken from the same mass differ from each other in composition, which is self evident, as it must be held impossible to divide homogeneously 0.2—0.4 weight percentage of water in the crystals.

In agreement with this the solubility figures in dry benzene also show divergencies. It is quite in agreement with the results of ERNST COHEN and VAN DOBBENBURGH's experiments that they give higher values than in the preparates which are crystallized from ether.

§ 6. Very instructive are the determinations with the preparates K and L; heating to 100°—105° C. is not sufficient to remove the occluded water completely.

The distinct difference in heat of combustion between the powdered preparete L and the preparete K, which was not powdered, further shows that powdering, as was to be expected, opens part of the capillary pores. No doubt it would be possible to obtain a preparete of about the exact heat of combustion by alternate powdered and heating.

§ 7. Furthermore we call attention to the conduct of preparete H, of whose previous history we know only that in the factory-works it was recrystallized from water. We are not acquainted with the further operations in the factory. Meanwhile it given values for the heat of combustion which are identical with those previously found by VERKADE and COOPS.

§ 8. Summarizing, we see that preparates finally recrystallized from water must never be used as standard-preparates, even after drying to constant weight in vacuo over P_2O_5 , or after heating for six hours to 100°—105° C., as they give values for the heat of combustion which must be considered as accidental.

On the contrary, preparates finally crystallized from dry ether give constant values, which are in good agreement with those found by VERKADE and COOPS for preparates which had been finally crystallized from ether or chloroform.

Summary.

It was demonstrated that, if salicylic acid is to be used as a "standard-substance" for the determination of the heat of combustion, the prescriptions for its preparation must be formulated more sharply — especially as regards the final crystallization — than was done up to this time. It was seen that

constant values which can be reproduced, can be expected only if the final crystallization has been made from dry ether. A special investigation will have to establish what other solvents may be used for this final crystallization.

The disturbances which occur when crystallizing from water can be accounted for by the presence of occluded water in the crystals, which cannot be completely removed, neither by drying in vacuo over P_2O_5 , nor by heating to 100° — 105° C. for six hours.

VAN 'T HOFF-Laboratory—

Laboratory of the Nederlandsche Handels-Hoogeschool.

Utrecht—Rotterdam, November 1925.

Histologie. — "*On the Histological Structure of Fibrous Substances.*"

By G. C. HERINGA and Miss H. A. LÖHR. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of February 27, 1926).

In a previous communication some of the reasons were given which led us to regard the cause of the collagenous fibres of the connective tissue as being gelatinization of a fibre-building colloidal solution („Stäbchen Sol" after Szegvari). Further research did but strengthen our conviction. The arguments which support this belief are partly negative, partly positive. As negative arguments serve all the observations of other writers which point to the origination of collagenous fibrils in the absence of cells, and in particular the impossibility of reconciling the architectonics of the fibrillar structure with the arrangement and development of the cells held by others as responsible for the formation of fibres. Especially in respect to this last point the classic observations of VAN EBNER have lost nothing of their value to us, while the better preservation of the structure by means of the gelatin freezing method has assisted our train of thought.

As positive arguments we had : 1. that, especially with the aid of dark-field microscopy and by making use of azimuth effect, we were able to study collagenous fibrils of visibly different thicknesses in the spaces between the cells, which waved in such a way, or even became confused into tangled knots, that there could be no question of a continuous contact with any cell area that might influence the thickness of the fibres individually. On the contrary, the morphological resemblance to the aspect afforded by other colloidal fibres (soap, benzopurpurine, and others) in gelatinization, where certainly no fibroblasts are functioning, is particularly striking. A second and, in our opinion stronger, argument was furnished us by a further similarity, namely, the inclination towards a parallel drawing together of the fibrils. This symptom, which appeared in varying intensity according to the special kind of the connective tissue we examined, proved to be entirely analogous to what SZEGVARI and ZOCHER have described for their substances. In this "bundling process" also specific influence from the cells may be precluded. It was along this path we thought we should arrive at a rational explanation of the bundle-like course of the collagenous fibres so familiar to the histologists of old in their preparations, and which appears again and again in innumerable connective tissue formations, and has hitherto been commonly ascribed to the expression of fibroblastic functioning.

It was naturally of importance now to our train of thought to know whether the same or analogous aspects are to be found again with other substances which, as appears from optical or röntgenographic examination, are related to collagen, i.e. substances which, as appears from double refraction, must likewise be regarded as built up from parallel crystalline micells, and are röntgenographically distinguishable by a 4-points diagram.

Our attention was especially directed to the chitin, and that for a very particular reason. In our examination of connective tissue we had come to the conclusion that the drawing together of the collagenous fibrils leads not merely to the formation of bundles of considerable thickness (which bundles, by-the-way, are never round, but invariably a flattened oval, or ribband-like), but that under certain circumstances dominates the coalescence in one plane in such a way that they must be termed true collagenous membranes (the "lamelles" described by LAGUESSE with so much emphasis, and somewhat over-estimated as to their significance in the construction of the connective tissue). This renders an analogy with the chitin directly obvious; for there too we find beside chitin tendons, the occurrence of the membranous cuticulae which, to judge from their appearance, would not at all remind us of a "fibre-diagram".

Thanks to the kindness of Dr. HIRSCH, of the Zoological Laboratorium, we had the use of several specimens of chitin, and now looked for a piece that, under the microscope with low power, showed no special structure (pleurite of an astacus).

The examination of this piece in dark field with azimuth lighting yielded the desired effect, finer than we had ventured to expect. It showed us the chitin build up by interwoven bindles of parallelly running fibrillae, differently orientated in consecutive layers; the latter particular, when the illuminating slit was revolved, yielded, for the azimuth effect, a highly beautiful and charming alternating play of light and shadow.

All previous studies of chitin had already confirmed the supposition long ago expressed as to its fibrous structure. Nevertheless the extreme clearness with which this structure can be seen by our method of investigation is, in our opinion, worth mentioning. But moreover, with reference to the complete accordance in structure, we would touch again upon the analogy with the connective tissue. Whereas in the case collagen a cytological explication of the structure could still, albeit with some difficulty, be based upon the presence of fibroblasts, this was felt to be a greater objection with regard to chitin which, as could not be doubted, makes its appearance as a fluid shapeless mass. In the bulky treatise which BIEDERMANN (*Handb. der Vergl. Physiologie*, III, 1914) has devoted to this subject, it is curious to note what complicated reasoning is required to make it plausible that some mysterious changes in the function of the chitinous cells must be the cause of the structure observed. (Conf. SCHMIDT. *Die Bausteine*, etc. Bonn 1924, pg. 195 sequ.)

But we have not arrived by a long way yet at an explanation of the

complicated image of the structure of chitin, no more than of the connective tissue. Only we wish to single out one fact from the total of the phenomena, namely, the common fibrilization of both and the inclination of the fibrils to form themselves into bundles.

These two phenomena, if our assumption of colloidal coagulation be accepted, may be eliminated from the proposition as directly attributable to the micellar properties of the substances. There then remains a second question to be answered separately, viz. that of the factors which govern the course of the bundles and their union in the form of tissue into more complicated systems of a higher order. The observations of colloids in vitro by the colloid-chemici have taught us nothing on this head. At the most they show the result of a mechanical influencing (streaming, cataphoresis) of the preparations by the appearance of structural lines in accordance with the direction of the acting force. That similar influences might well be the cause of polar differentiation in living nature also (according to VAN EBNER's hypothesis of tension) has been irrefutably determined by ROUX' expositions, and by LEVY's experiments on tendon regeneration. Equally certain it is, however, that this explanation absolutely fails in a number of cases. Especially we refer here to the arrangement in layers, with a course intersecting in more or less sharp angles, a peculiarity which, remarkably enough, crops up throughout the entire organism of nature in the most dissimilar fibrous substances. We have just remarked how far-fetched it is to ascribe this phenomenon in the case of chitin, where no cells occur between the layers, to a charge of secretory function. BIEDERMANN is undoubtedly right, however, in saying that a consistent working out of the theory of tension would likewise lead *ad absurdum*. Well, then, the same holds good equally for the connective tissue, as, for example, appears from the fact that in the thin layers of LAGUESSE fine alternating layers are still to be seen.

Here, then, we find ourselves confronted by a still unsolved puzzle. All the more, we ask ourselves whether the alternating layers of fibrous substance, so frequently met with, are caused, like the bundling principle by the micellar properties of the substance itself. Possibly the colloid-chemistry, with its ever-advancing results, may throw some light on this too in the future.

Histology. — "*On the form and conjunction of the involuntary muscle-fibres of mammals.*" By G. C. HERINGA. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of February 27, 1926).

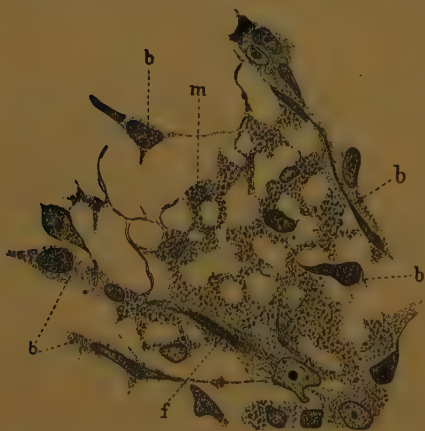
That the involuntary muscle-fibres in mammals have not by any means invariably the smooth spindle shape which is generally met with in isolation preparations and in text-book illustrations, but that on the contrary rammified forms, also in warm-blooded animals, are oftener the rule than the exception, is a conviction which is firmly grounded upon the genetic connection which, as appears from the researches of MC. GILL, exists between mesenchyma and smooth muscle-cells. KOELLIKER, in fact, has already given us beautiful pictures of isolated cells, which in principle clearly show this branching in the form of more or less blunt splitting at the points.

In the discussions as to whether the muscle-cells are united with each other, it has long been a point of dispute whether or not protoplasmatic paths occur, and finally it has been agreed that the fine indentations which are frequently to be seen on the edge of the cross-sections and which led to a belief in the plasmodesma, are indeed artefacts, or products of shrivelling.

But the observations of LEVI of muscle-cells in vitro, whereby the passage

of the fibrils from cell to cell could be observed with absolute certainty, have determined more surely than ever that there is a direct protoplasmatic continuity by genuine cell-processes. We must thus assume that the smooth muscle-cells, just as the connective tissue cells and the heart-muscle cells, are connected with each other in a three-dimensional network. In the close layers of smooth muscular tissue this is not seen owing to the dense crowding of the elements. The accuracy of the supposition, however,

becomes perfectly clear in the more loosely built involuntary muscles. The accompanying illustration shows a portion of the muscularis mucosae of the intestine of a cat, fixed with Susa (HEIDENHAIN), and cut according to the gelatin freezing method.



The muscle-cells (*m*) have here preserved their branched form and reticular syncytium, as illustrated by MC. GILL in her embryonal preparations. Only in the strongly refracting fibrillae surrounded by their protoplasm are they distinguishable from the connective tissue cells (*b*) lying between them. A few connective tissue septa (*f*) of fibrillar form have pushed their way in between. The spaces between the meshes of the cells are filled up by a barely visible gelatinous mass united directly to the cells.

Further research will be required to elucidate the mutual relationship between the muscle-cells on the one hand and the connective tissue and the intermediate substance on the other.

Geology. — "*The structure of the Sierra Nevada*"¹⁾. By Prof. H. A. BROUWER.

(Communicated at the meeting of March 27, 1926).

According, to one of the recent publications on the structure of the Sierra Nevada²⁾, the Alpine mountain-building has but caused the great geanticline of the existent mountains, without forming any important foldings. Explorations in the central part of the Sierra de los Filabres^{3, 4)}, the eastern prolongations of the Sierra Nevada have shown the existence of large overthrusts in this part of the betic ranges, proving a movement in a northern direction. Our explorations were continued in the western part of the Sierra Nevada and resulted in determining large overthrusts also in this region, and therefore in concluding to a similarity in structure in a large part of the betic mountains with the Alps. Just as in the Sierra de los Filabres, we can distinguish in the Sierra Nevada a central part, consisting of crystalline schists, from a border zone, where triassic sediments predominate. Fossils were not found here, but the limestones are like those of the Sierra de Gador, the Sierra de los Filabres and the Alpujarras, where *Myophoria*, *Monotis*, *Avicula*, *Mytilus* and *Megalodon* have been found. BARROIS and OFFRET⁵⁾ have distinguished pre-Cambrian, Cambrian and Triassic in the Sierra Nevada and the Alpujarras. Later explorers^{6, 7)} consider a part of the Cambrian sediments to be Triassic, while ranging the pre-Cambrian sediments as pre-Triassic, without a definite determination of their age. They presume an important unconformity between Triassic and pre-Triassic sediments, but we did not find any unconformity in the Sierra Nevada and take the unconformable succession, observed locally and rarely in adjacent regions, to be a tectonic unconformity. Also the relict structure of the Sierra de los Filabres formerly

1) Some additions to the original paper have been made after a recent visit to the region.

2) J. CARANDELL. La morfología de la Sierra Nevada, ensayo de su interpretación tectónica. Madrid 1921.

3) H. A. BROUWER and C. P. A. ZEYLMANS VAN EMMICHOVEN. The tectonics of the central part of the Sierra de los Filabres. (South Spain). These Proceedings 28, 55.

4) C. P. A. ZEYLMANS VAN EMMICHOVEN. Geologische Onderzoekingen in de Sierra de los Filabres. Proefschrift. Delft. 1925.

5) CH. BARROIS et A. OFFRET. Mémoire sur la constitution géologique du sud de l'Andalousie de la Sierra Tejada à la Sierra Nevada. Mission d'Andalousie. Mém. Acad. des Sciences. Tome XXX, N^o. 2, 1889.

6) C. P. A. ZEYLMANS VAN EMMICHOVEN. loc. cit.

7) W. A. HETZEL. Bijdrage tot de geologie van de Sierra Alhamilla. Proefschrift. 's-Gravenhage 1923.

described by us¹⁾ may have been caused by deposition in a basin of sedimentation with a hercynic direction. In any case, the structure shows a strong resemblance to the penninic regions of the Alps, where slight hercynic elevations were existent and denuded before the Triassic, but where the Triassic transgression is but rarely found and is slightly unconformable on the older sediments. It is nearly always a parallel-transgression.

We therefore believe that there is no reason to suppose an important stratigraphic break and the absence of the late-Palaeozoic. While exploring in the Sierra Nevada we found a zone between the Triassic and the crystalline schists, characterized by micaceous marbles, slates, quartzites, lime-bearing sandstones and marls, muscovitegneisses with felspar-eyes, tourmaline- and garnet-bearing gneisses, amphibolites and micaschists, which often contain garnet. Also serpentine is sometimes found in this zone. This zone often shows a very complicated structure, which will be dealt with hereafter; some sediments bear a resemblance to Triassic in metamorphic state, others might very well be of Permian age, while crystalline schists, which are found nearer to the central parts of the Sierra could belong likewise — anyway partly — to the late-Palaeozoic. Some authors suppose the occurrence of "Bündner Schiefer" (schistes lustrés) in the Sierra Nevada. The lack of lime in the crystalline schists of the central part of the mountain is in our opinion against this supposition, at least if this name is used for metamorphic mesozoic sediments. But in the above-mentioned zone, between the Triassic border-zone and the crystalline schists of the central part of the mountain range, marbles with alternating beds of schist, which are very similar to the mesozoic "Bündner Schiefer" are sometimes found. An exact stratigraphy of the crystalline schists cannot be made without future explorations and for the present we will distinguish subsequently from the border to the central parts of the Sierra Nevada the following zones:

1. *Triassic* (limestones and dolomites, silky slates, sandstones and quartzites, gypsum, rauchwackes) and older rocks.

2. *Mixed zone* (micaceous marbles, slates and quartzites, lime-bearing sandstones and marls, muscovite-bearing gneisses with felspar-eyes, tourmaline- and garnet-bearing gneisses, amphibolites and micaschists, often bearing garnet). Pre-Mesozoic and older-Mesozoic.

3. *Crystalline schists* (partly garnetiferous micaschists, locally amphibolites and serpentine).

The rocks of the mixed zone resemble in many respects to part of the rocks of the "zone des schistes lustrés" in the Alps. Without entering further into the stratigraphic relation — the judgment of which cannot be final, because it should be derived from the petrographic characteristics of metamorphic sediments without fossils —, we consider now the tectonic relation between the three zones, which was studied by us at various

¹⁾ H. A. BROUWER and C. P. A. ZEYLMANS VAN EMMICHOVEN. loc. cit.

places. In another paper ¹⁾ we gave a more extensive description of our results, confining them here to some general conclusions about the structure of this part of the betic ranges.

Structure of the "mixed zone".

In this zone complicated folding can be traced, especially in the mica-bearing marbles. In the Cerro del Cardal near La Calahorra, S. of Guadix, the folds are dipping in a N. direction, while at the base of the micaceous marbles an overthrust-breccia is found at different places. The quartzites of the mixed zone are locally stowed to great thicknesses, while further to the N. there are but small isolated lenses of quartzites in the blue slates, on which the micaceous marbles could easily slide forward. To the E. of Niguelas, at the western border of the Sierra, the mixed zone is equally disturbed by folding and overthrusting, special layers can often be followed for a short distance only and are thinning out as well in the direction of the strike as in that of the dip. We found similar relations at other places along the N. and S. border of the Sierra, and the mixed zone gives the impression of being a series of sediments characterized by strong lamination and overthrusting between the crystalline schists of the central part of the Sierra and the Triassic.

Crystalline schists in the border-zone and in the Alpujarras.

The sometimes garnetiferous crystalline schists in the central Sierra Nevada are not confined to this central part. We found them to the S.E. of Granada near the village Monachil, as well N. as S. of the Rio Monachil. They rest with varying strike and dip upon the strongly disturbed Triassic limestones in the vicinity of the Tertiary of the basin of Granada. Also in the more central parts of the Triassic border-zone sediments of the same kind have been found further to the E. near the path, which leads to the Picacho de Veleta, W.N.W. of the Cortijo de Membris ²⁾.

To the S. and S.W. of Lanjaron, near the border of Sierra Nevada and Alpujarras we found in the crystalline schists isolated blocks of crystalline limestones, which are limited by tectonic contacts, while the Triassic limestones, which form a large syncline S. of Lanjaron are covered by phyllitic rocks and, sometimes garnetiferous, micaschists. These garnetiferous micaschists have also been found between Ugijar and Mairena in a region where Triassic sediments prevail. In the Alpujarras, farther south, several large windows („Fenster") of Triassic limestones and slates, covered by garnetiferous micaschists have been found (e.g. window of Albunol, window of the Cerrón etc.).

The above mentioned examples may be sufficient proof, that the

¹⁾ H. A. BROUWER. Zur Geologie der Sierra Nevada. Geol. Rundschau. April 1926.

²⁾ It has been found since, that they have an extensive development resting upon and also dipping below the Triassic limestones and slates to the east of the basin of Granada.

connection between the Triassic border-zone and the central crystalline schists cannot be simply considered to be an older nucleus of which the later sediments in the most upheaved parts have been removed by erosion. The crystalline schists have been found far to the south of the central part and were pushed to the north of it by very important horizontal movements.

Repeated occurrence of the rocks of the mixed zone.

At both sides of the Rio Monachil in the N.W. part of the Sierra Nevada, about 1 K.M. up river from the mixed zone between the Triassic and the crystalline schists, another series of strata is found, which is characterized by the existence of micaceous marbles, tourmalinegneiss, amphibolites, serpentines etc. Marly limestones with intrusive dioritic to amphibolitic rocks were also locally found E. of Niguelas, in the western part of the Sierra, about 1 K.M. to the E. of the mixed zone in the Barranco del Torrente. Likewise at different other places in the central part of the Sierra serpentine and amphibolites were found.

The tectonic significance of these repeated occurrences can for the present not be exactly determined.

The tectonics of the late-Tertiary.

S. of the Sierra Nevada the village Ugijar is situated in a Tertiary basin, which consists, according to BARROIS and OFFRET, of miocene lake-deposits. This Tertiary is folded in anticlines and synclines, in the N. part the Triassic is uncovered between the younger sediments and in a syncline between Ugijar and Mairena, along the N. border of the basin, dip and strike are strongly varying, the northern limb shows a very steep dip of the strata, locally these are overfolded at the contact with the Triassic.

The Tertiary is also folded along the W. border of the Sierra. In the vicinity of Monachil, at the N.W. border, the strata dip away from the Triassic border-zone. We likewise located steep dips S. of the Rio Monachil. Dips of 50° — 60° and even vertical or overfolded position of the strata were observed at the contact with the Triassic in Tertiary sandstones and conglomerates.

Summary.

All these results give ample proof, that the structure of the Sierra Nevada, as well as that of the eastern continuation has — as has been supposed already by several authors ¹⁾ — a strong similarity with the structure of

¹⁾ P. TERMIER. Les problèmes de la géologie tectonique de la Méditerranée occidentale. Rev. gén. des Sc. t. 22. 1911. L. GENTIL. Sur l'origine des nappes de recouvrement de l'Andalousie. Comptes Rendus Acad. des Sciences. T. 167. 1918, p. 238. E. ARGAND. Des Alpes et de l'Afrique. Bull. Soc. Vaudoise des Sc. Nat. Vol. 55, 1924, p. 233. E. ARGAND. La tectonique de l'Asie. C. R. Congr. Géol. Int. XIII session. 1922. R. STAUB. Der Bau der Alpen. Beitr. zur geol. Karte der Schweiz. N. F., 52 Lief. p. 250. 1924.

the Alps, of which the betic ranges may be considered to be a direct continuation.

Because of the lack of a clear unconformity between Triassic and prae-Triassic sediments the Sierra Nevada bears a resemblance to the penninic or axial zone of the Alps. In the N. as well as in the S. part of the Sierra the Triassic border zone and the mixed zone have a very complicated structure, principally denoting large overthrusts in a N. direction, which direction of movement is also indicated in the crystalline schists of the central part. Crystalline schists, similar to those of the Alpujarras, being existent till near the outer border of the northern Triassic border-zone, these movements must be very intensive.

One of the windows in the Alpujarras (window of Albunol) proves already a slip of one of the overthrusts in these mountains of at least 7 kilometers. The roots of the overthrust sheets in the Triassic rocks and crystalline schists of the northern border-zone of the Sierra Nevada have to be looked for to the south of the Sierra in the Alpujarras, where similar rocks are found. Where the highest parts of these overthrust sheets, which can be compared with the lower "East-Alpine overthrust sheets" of the Alps have been eroded away, the crystalline schists of the central part of the Sierra Nevada are uncovered and form the highest peaks of the mountain range. Between these lower "East-Alpine overthrust sheets" and the crystalline schists of the central part the mixed zone is found, which is characterized by a higher crystallinity of its rocks, if compared with the crystalline schists of the central part, upon which they rest, while the rocks resemble in many respects those of the "zone des schistes lustrés" of the Alps. Although different in many respects, the structure remembers that of the Hohe Tauern in the Eastern Alps, where a penninic window, surrounded by the "East-Alpine overthrust sheets" is uncovered by erosion ¹⁾.

That the movements have continued after the formation of these structures is proved by the great uplift of the present mountain range and by the sometimes very steep dips and overfolded position of the late-Tertiary deposits, which have not been eroded away in the marginal parts of the mountain range only.

¹⁾ Proofs of the existence of higher overthrust sheets, of which the roots have to be looked for to the south of the Alpujarras (Mediterranean) have been found this summer. In the region between Nivar and Diezma to the north-east of Granada the overthrust sheets with the Triassic in Alpine development dip below the sediments of the sub-betic chains, where the Triassic is found in the more continental development with reddish sandstones, shales and conglomerates.

Physics. — “On the Equation of State of Solid Substances etc., in Connection with the General Expression for the Energy and the Entropy. Simple Derivation of the So-called Entropy Constant.”
 III. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of March 27, 1926).

I

The Energy.

1. General Considerations.

In our foregoing paper we have made use of DEBYE's well-known expression for the Energy of a *solid substance*, viz. — with the addition of the terms referring to the potential Energy of the attractive and (static) repulsive forces:

$$E = \frac{9RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx + \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv, \quad (1)$$

in which x_m is $= \frac{\beta v_m}{T} = \frac{\theta}{T}$. The quantity θ occurring there (the so-called “characteristic” temperature) is given by equation (4) of the paper mentioned, viz.

$$\theta = C v^{2/3} \sigma_1^{-1/2}, \quad (2)$$

in which C is $= 0,0025 f M^{-1/2}$. In this f is a factor containing the so-called POISSON modulus (to be replaced in gases and liquids by $\sqrt{c_p : c_v}$). Through $\sigma_1 = - \left(\frac{dv}{dp} \right)_t$ the value θ will, therefore, in general still be a function of T and v .

We have seen that as long as $p=0$ for solid substances, the quantity θ varies but little between the absolute zero and the ordinary temperature. (for copper e.g. from 331 to 321; see § 5 of Chapter IV of the foregoing Paper). When p approaches to ∞ , in which the extreme limiting volume v_{00} is reached, θ will rapidly approach ∞ , because then the coefficient of compressibility $\sigma = - \frac{1}{v} \left(\frac{dv}{dp} \right)_t$ draws near to 0. Hence we have for solid substances (e.g. copper):

$$x_m = \frac{\theta}{T} = \frac{330 \left(\frac{p=0}{v=v_0} \right) \text{ till } \infty \left(\frac{p=\infty}{v=v_{00}} \right)}{T}.$$

At comparatively high temperatures (not too far below the meltingpoint) x_m will, therefore, be comparatively *small* at ordinary pressures, so that then the above formula (1) will fall, as regards the development into series, in the so-called RT -region ($E = 3RT \dots + \text{Pot.}; p + \frac{a}{v^2} = \frac{\lambda/v + RT \dots}{v-b}$) (on the right of the line A in the subjoined Fig. 1). But at *very high*

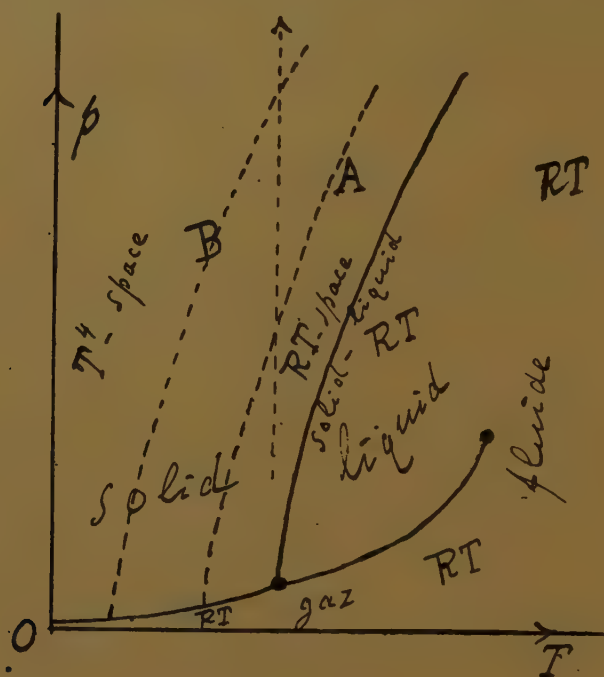


Fig. 1.

pressures x_m becomes great, and we shall gradually get, as regards the development into series, in the so-called T^4 -region:

$$\left(E = \frac{9}{8} R\theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_a^3} T^4 \dots + \text{Pot.}; p + \frac{a}{v^2} = \frac{\lambda/v + PT^4 \dots}{v-b} \right)^{1)}$$

(on the left of line B; the part between A and B represents the intermediary region, in which neither the development into series for small values of x_m , neither that for large values of x_m is valid, so that there the general formula (1) would have to be used).

At *very low temperatures* we shall, of course, always be (in the solid state) in the T^4 -region (on the left of B), also at ordinary pressures.

1) θ_a denotes the value of θ at $T=0$; this is, accordingly, still a function of v ($\theta^2 = \theta_a^2 (1 + \varphi_1 T^4 \dots)$; cf. foregoing Paper p. 170). θ_0 is supposed independent of v .

For *liquids*, where Θ is smaller than for solid substances, and T higher, we shall always be in the RT -region, unless at very high pressures we should cross the line A , i.e. in the case that this line cuts the line of liquid-solid.

And finally for *gases* we shall *always* be in the RT -region, however low the temperature should become, and even at 0. This is very essential, because the opposite view has also been held, and the consequences of this, e.g. with regard to the Entropy are very far-reaching.

That what has been said is correct, will be clear on the following considerations. For gases the quantity θ is exceedingly small at the ordinary pressures, as at higher temperatures $\sigma_1^{-1} = - \left(\frac{dp}{dv} \right)_t = \frac{RT}{v^2}$

follows from $p = \frac{RT}{v}$, so that then the quantity θ becomes $= C \frac{\sqrt{RT}}{v^{1/3}}$

on account of (2), hence $x_m = \frac{\theta}{T} = \frac{C\sqrt{R}}{T^{1/2}v^{1/3}}$, in which T is great and v very great. And at *high pressures* the same thing holds for the *fluid* region as we have said before of the liquid phase.

How will all this be for gases at *very low temperatures*? Then the quantity θ will be either proportional to \sqrt{T} : $v^{1/3}$, or to T^2 : $v^{1/3}$, according as one supposes to be in the RT -region or in the T^4 -region.

Hence the quantity $x_m = \frac{\theta}{T}$ with $\frac{1}{T^{1/2}v^{1/3}}$ or with $\frac{T}{v^{1/3}}$. In the latter case, however, x_m would verge to 0 at T very small and v very great; i.e. one is then not in the supposed T^4 -region, but in the RT -region. And in the former case — as even on the saturation line solid-vapour it follows from the vapour-pressure-equation that v increases in a much greater degree (and that *exponentially*) with T than T decreases, so that even at $T=0$ x_m will still approach to $1:(0 \times e^\infty)$, i.e. to 0 — this will be the case in a much greater degree *below* the said saturation line, where v is still much greater (∞ at $p=0$ on the T -axis).

We have, therefore, proved that in the *solid* state the T^4 -region exists only on the *left* of a certain line B , and that for *liquids* and *gases* we are *always* in the RT -region, even if the temperature (for gases) verges to 0. For in the first case x_m is comparatively *great*, so that the development into series with T^4 etc. is valid; in the second case x_m is comparatively *small*, so that the development into series with RT etc. will be applicable.

Hence, whether one has the first case or the other, does not depend only on T , but also on the quantity θ , which will depend in a pretty great degree on T and v . For it is after all only the value of $x_m = \theta:T$ that is decisive, and not that of T .

We will just remark that in the above equation (1) not λ has been written, but λ/v , in accordance with Note 1) to § 2 of Chapter II of the foregoing Paper, because otherwise the potential Energy of the

(static) repulsive forces would become infinite already for finite values of v . For gases, where (at ordinary pressures) v is very great, this term, like a/v^2 , disappears naturally. For liquids and gases the expression for E must further still be divided by 2.

It may further still be mentioned that in the Figure we have assumed the possibility of an (exceedingly small) *zero-point pressure* at the equilibrium solid-vapour. This will be rendered probable in the following Paper.

2. Equation of Energy and Equation of State in the RT -Region (x_m small).

Though we already made some remarks on this subjects in our foregoing Paper, we will now come back to it to discuss, what was treated there, somewhat more at length.

For small values of x_m we may write for (1) (when nothing else is stated, it is supposed that we have to do with *solid* substances; the slight modifications for the liquid and gas state have already been indicated above):

$$E = \frac{9RT}{x_m^3} \left[\frac{1}{8} x_m^4 + \left(-\frac{1}{8} x_m^4 + \frac{1}{3} x_m^3 + \frac{1}{60} x_m^5 - \frac{1}{5040} x_m^7 \dots \right) \right] + \text{Pot. Energ.}$$

It is seen from this that the term corresponding to the zero-point energy $\frac{1}{8} x_m^4$ is cancelled by the term ensuing from the integration of the piece with $e^x - 1$, i.e. $-\frac{1}{8} x_m^4$, so that the zero-point energy will no longer occur in the expression for E at higher temperatures (i.e. small values of x_m), which comes to this that E will then duly approach to RT , without the addition of a constant term without T which remains *finite*. We, therefore, get simply with $x_m = \theta : T$:

$$E = 3RT \left[1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} \dots \right] + \text{Pot. Energ.}$$

But as $\theta^2 = \theta_a^2 \left(1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right)$, in which φ_1, φ_2 etc. are still functions of v (see the foregoing Paper, Chapter I § 3), the above development into series with exclusively even powers of T^{-1} will pass into one with all whole powers of T^{-1} , i.e. it will be of the form:

$$E = 3RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3} \dots \right) + \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv \quad (x_m \text{ small}), \quad (3)$$

in which A will be $= \frac{1}{20} \theta_a^2 \varphi_1$; $B = \frac{1}{20} \left(\theta_a^2 - \frac{1}{84} \theta_a^4 \varphi_1^2 \right)$; etc. The quan-

ties θ_a, φ_1 , etc. can be calculated from the coefficient of compressibility occurring in the equation (2) of § 1. And this coefficient can in its turn be derived from the equation of state. It is, therefore, of the highest importance accurately to know the form of this latter equation in connection with (3). All this has already been set forth at length in our preceding Paper, but we wish to give some more generality and extension to it here.

As it is known, the following purely *thermodynamic* relation holds for E :

$$E = \int_{\infty}^T c_v dT + \int_{\infty}^v \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv + E_{T=\infty, v=\infty} \quad (4)$$

in which we have, of course, chosen ∞ for the lower limit of T , and not 0, because (3) is only valid for small values of x_m (high values of T). With regard to v , we might also have chosen $v = v_{00}$ for lower limit; $E_{T=\infty, v=\infty}$ would then have become $E_{T=\infty, v=v_{00}}$. We draw attention to this, that according to a theorem proved in our foregoing Paper (chapter II, § 1, Note 1) concerning the integration between definite limits of *total* differentials (here dE), either at the limit of the *first* integral what stands under it must be taken at the lower (constant) limit of the *second* integral; or inversely at the second integral what stands under it at the lower (constant) limit of the *first* integral.

For c_v the following equation evidently holds according to (3):

$$c_v = \left(\frac{dE}{dT} \right)_v = 3R \left(1 - \frac{B}{T^2} - \frac{2C}{T^3} \dots \right),$$

so that $c_{v=\infty}$ becomes $= 3R$, as the coefficients B, C , etc. (see our preceding Paper) all become $= 0$ at $v = \infty$.

We may, therefore, write for p :

$$p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \frac{RT}{v-b} \left(1 + \frac{P'}{T} + \frac{Q'}{T^2} + \frac{S'}{T^3} \dots \right),$$

or also:

$$p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \frac{RT}{v-b} + R \left(P + \frac{Q}{T} + \frac{S}{T^2} \dots \right) \quad (5)$$

in which the coefficients P, Q, S , etc. are in general still functions of v , and can be expressed from the above thermodynamic relation (4) in A, B, C , etc. We now get:

$$T \left(\frac{dp}{dt} \right)_v = \frac{RT}{v-b} - R \frac{Q}{T} - 2R \frac{S}{T^2} \dots,$$

hence

$$T \left(\frac{dp}{dt} \right)_v - p = \frac{a}{v^2} - \frac{\lambda/v}{v-b} - RP - 2R \frac{Q}{T} - 3R \frac{S}{T^2} \dots,$$

so that we may now write:

$$E = 3R(T - T_{\infty}) + \left[-\frac{a}{v} - \int_{\infty}^v \frac{\lambda/v}{v-b} dv - R \int_{\infty}^v P dv - \frac{2R}{T} \int_{\infty}^v Q dv - \frac{3R}{T} \int_{\infty}^v S dv \dots \right] + E_{T=\infty}.$$

In this the quantity $E_{T=\infty}$ is evidently $= 3RT_{\infty} + \frac{a}{v_{00}}$ (the potential energy of the (static) repulsive forces disappears at $v = \infty$), so that the following equation is obtained:

$$E = 3RT - R \int_{\infty}^v P dv - \frac{2R}{T} \int_{\infty}^v Q dv - \frac{3R}{T} \int_{\infty}^v S dv \dots + \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv.$$

If this is compared with (3), the following equations follow immediately:

$$\underline{P = -3 \cdot \frac{dA}{dv}}; \quad \underline{Q = -3 \cdot \frac{1}{2} \frac{dB}{dv}}; \quad \underline{S = -3 \cdot \frac{1}{3} \frac{dC}{dv}}; \text{ etc.,} \quad (6)$$

(all the differentiations with respect to T const.), through which the additional terms at $\frac{RT}{v-b}$ in the equation of state (5) have been brought in connection with the corresponding additional terms at $3RT$ in the Energy equation (3). If, therefore, A, B, C , etc. are functions of v — and this is the case in the theory of DEBYE, because θ depends, besides on T , in a great degree on v — also the equation of state will necessarily contain terms of “degeneration”. It appears from the above that those terms with P, Q, S etc. will in general not be equal to those with A, B, C etc. This is only the case with ideal gases; then P becomes $= A$, $Q = B$, etc., as may be read in my preceding Paper.

If in general

$$E = \omega + \text{Pot. Energ.}; \quad p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \varphi,$$

in which, therefore, ω and φ are two different functions of T , it appears from the above derivation that generally $\left(\varphi' \text{ means } \left(\frac{d\varphi}{dt} \right)_v \right)$ must be:

$$T\varphi' - \varphi = \left(\frac{d\omega}{dv} \right)_t \dots \dots \dots (6^a)$$

This follows, of course, also from the well-known relation $\left(\frac{dc_v}{dv} \right)_t = -T \left(\frac{d^2p}{dt^2} \right)_v$, yielding $\left(\omega' \text{ means } \left(\frac{d\omega}{dt} \right)_v \right) \left(\frac{d\omega'}{dv} \right)_t = T\varphi''$, i.e. $\left(\frac{d\omega}{dv} \right)_t = T\varphi' - \varphi$.

If, therefore, ω is no function of ν , as in the earlier, simple PLANCK-EINSTEIN theory, then $T\varphi' - \varphi = 0$. The quantity φ will then simply be $= f(\nu) \times T$ (in our case $\frac{RT}{\nu - b}$), and in the equation of state degeneration-terms could *never* occur at finite values of T . This, accordingly, condemns the said PLANCK-EINSTEIN theory.

N.B. In our preceding Paper we have kept the first integral in (4) general, and the second at $T = \infty$; this, however, only gives P expressed in A (cf. Chapter II, § 2 and 3), whereas Q, S etc. must then still be expressed in B, C etc. by means of the equation with $\left(\frac{dc_\nu}{d\nu}\right)$. Hence this method is less simple than the above, more direct one.

In the above we may also take the limiting volume ν_{00} as lower limit of ν (we already alluded to this above), but this too would complicate matters, though the result remains entirely the same.

3. Equation of Energy and of State in the T^4 -Region (x_m great).

For great values of x_m (see also our preceding Paper) follows from the general equation (1):

$$E = \frac{9}{8} R\theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_a^3} T^4 + \dots + \text{Pot. Energ.},$$

in which θ_a is the value of θ at $T=0$ (hence still $= f(\nu)$), θ_0 being the value for $T=0$, $\nu=\nu_0$. Hence we have, when $\frac{9}{8} R\theta_0 = E_0$ (the so-called zero-point energy), $\frac{3}{5} \frac{R\pi^4}{\theta_a^3} = A$, etc. is put:

$$E = E_0 + AT^4 + BT^8 \dots + \left(\frac{a}{\nu_{00}} - \frac{a}{\nu} \right) - \int_{\infty}^{\nu} \frac{\lambda/\nu}{\nu - b} d\nu \quad (x_m \text{ great}), \quad (7)$$

in which A, B etc., i.e. all (through θ_a etc.) are still functions of ν .

For the equations of state we can write in this case:

$$p = -\frac{a}{\nu^2} + \frac{\lambda/\nu}{\nu - b} + PT^4 + QT^8 \dots, \quad (8)$$

in which P, Q etc. will be functions of ν , which by means of the thermodynamic equation (4), now in the form

$$E = \int_0^T c_\nu dT + \int_{(\nu=\nu_{00})}^{\nu} \left(T \left(\frac{dp}{dt} - p \right) d\nu + E_{T=0} \right),$$

we shall express in A, B , etc.

We now have for c_v :

$$c_v = 4AT^3 + 8PT^7 \dots, \text{ hence } c_{v_0} = 4A_0T^3 + 8B_0T^2 \dots,$$

in which, therefore, A_0, B_0 etc. represent the values of A, B etc. at $v=v_{00}$.
Further

$$T\left(\frac{dp}{dt}\right)_v = 4PT^4 + 8PT^8 \dots,$$

hence

$$T\left(\frac{dp}{dt}\right)_v - p = \frac{a}{v^2} - \frac{\lambda/v}{v-b} + 3PT^4 + 7QT^8 \dots,$$

and therefore:

$$E = (A_0T^4 + B_0T^8 \dots) + \left[\left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{v_{00}}^v \frac{\lambda/v}{v-b} dv + 3T^4 \int_{v_{00}}^v P dv + 7T^8 \int_{v_{00}}^v Q dv \dots \right] + E_{T=0}.$$

In this $E_{T=0}$ is evidently $= E_0 - \int_{v_{00}}^v \frac{\lambda/v}{v-b} dv$ (now the potential energy of the attractive forces disappears at $v=v_{00}$), so that we get:

$$E = E_0 + \left(A_0 + 3 \int_{v_{00}}^v P dv \right) T^4 + \left(B_0 + 7 \int_{v_{00}}^v Q dv \right) T^8 \dots + \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{v_{00}}^v \frac{\lambda/v}{v-b} dv.$$

And from this follows immediately by comparison with (7):

$$\underline{P = \frac{1}{3} \frac{dA}{dv}}; \quad \underline{Q = \frac{1}{7} \frac{dB}{dv}}; \text{ etc., } \dots \dots \dots (9)$$

(the differentiations with respect to v again to be taken at T constant),

for then becomes e.g. $A_0 + 3 \int_{v_{00}}^v P dv = A_0 + 3 \cdot \frac{1}{3} (A - A_0) = A$; etc.

Also at low temperatures (large values of x_m) the coefficients P, Q etc. in the equation of state depend, therefore, in a very definite way on the coefficients A, B , etc. of the equation of Energy; in which in general (comp. § 2) $\left(\frac{d\omega}{dv}\right)_t$ will again be $= T\varphi' - \varphi$, they again *not* being equal to each other.

Recapitulating, we have for the Energy ($x_m = \Theta : T$):

$$\left\{ \begin{array}{l} E = 3RT \left(1 + \frac{A}{T} + \frac{B}{T^2} \right) + \text{Pot. Energ. } (x_m \text{ small : } RT\text{-region}). \\ E = \frac{9RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx + \text{Pot. Energ. (general)}. \\ E = E_0 + (AT^4 + BT^8 \dots) + \text{Pot. Energ. } (x_m \text{ great : } T^4\text{-region}). \end{array} \right.$$

(Occurs only for solid substances at low temp.; cf. Fig. 1).

In this A , B , etc. are still functions of v , and the Pot. Energ. is everywhere $= \left(\frac{a}{v_0} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv$. The coefficients P , Q , etc. of the equations of state (5) and (8) are dependent on A , B , etc. by means of the simple relations (6) and (9).

II

The Entropy.

1. The Entropy in the T^4 -region (x_m great).

In the calculation of the Entropy greater difficulties, chiefly on account of the so-called "Entropy constant", are to be surmounted than in that of the Energy. What we have found above in Chapter I concerning the equation of Energy, is now required for the calculation of the Entropy from the *thermodynamic* relation holding for it, because we cannot draw up the expression for the Entropy — as was the case with the Energy in equation (1) — in an independent way outside statistic, i.e. thermodynamic considerations.

We now start with the T^4 -region, because this presents no difficulties. This region is — see Fig. 1 — exclusively assigned to the *solid* state. As we have shown, it does not occur for liquids and gases, unless at exceedingly high pressures. As

$$dS = \frac{dQ}{T} = \frac{dE + p dv}{T} = \frac{dE}{T} + \frac{p}{T} dv,$$

in which $dE = c_v dT + \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv$, we have also

$$dS = \frac{c_v}{T} dT + \left(\frac{dp}{dt} \right)_v dv,$$

and hence

$$S = \int_0^T \frac{c_v}{T} dT + \int_{v_{00}}^v \left(\frac{dp}{dt} \right)_v dv + S_{T=0, v=v_{00}},$$

in which we have chosen the natural limits 0 and v_{00} as lower limits for the two integrals, and have further taken what stands under the second integral at the *lower* limit of the first integral, according to a theorem proved by me in the foregoing Paper. (See also above with the Energy). We might also inversely have taken the first integral at $v = v_{00}$, but this would have been more complicated; the result remains, of course, exactly the same.

From $c_v = 4AT^3 + 8BT^7 \dots$ and $\left(\frac{dp}{dt} \right)_v = 4PT^3 + 8QT^7 \dots$ (comp. § 3 of Chapter I) follows therefore:

$$S = \int_0^T (4AT^2 + 8BT^3 \dots) dT + \int_{v_{00}}^v 0 \cdot dv + 0,$$

because $\left(\frac{dp}{dt} \right)_v$ disappears at $T=0$, and also the Entropy at the absolute zero and at the extreme limiting volume must necessarily disappear, as then the probability of the appearance of a molecule or atom in the elementary limiting space $v_{00}:N$ has become the unit, and accordingly the log. of it $=0$. Hence there remains simply:

$$\underline{S = \frac{4}{3}AT^3 + \frac{8}{7}BT^7 \dots \left(\begin{matrix} T^4\text{-region} \\ x_m \text{ great} \end{matrix} \right)}, \quad \dots \quad (10)$$

which, therefore, duly becomes $=0$ for $T=0$. As long as T is not yet absolutely $=0$, S will still be dependent on v through A and B , though in a very small degree.

2. The Entropy in the RT -region (x_m small).

This case comprises the entire gas- and liquid states, and besides also part of the solid state at comparatively higher temperatures (Fig. 1, right of A). Let us now write:

$$S = \int_{\infty}^T \frac{c_v}{T} dT + \int_{v_{00}}^v \left(\frac{dp}{dt} \right)_v dv + S_{T=\infty, v=v_{00}},$$

then with $c_v = 3R \left(1 - \frac{B}{T^2} - \frac{2C}{T^3} \dots \right)$ and $\left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} - R \frac{Q}{T^2} - 2R \frac{S}{T^3} \dots$

(see § 2 of Chapter I) the equation becomes:

$$S = \int_{\infty}^T \left(\frac{3R}{T} - 3R \frac{B}{T^3} - 3R \frac{2C}{T^4} \right) dT + \int_{v_{00}}^v \frac{R}{v-b} dv + S_{T=\infty, v=v_{00}},$$

because at $T=\infty$ the terms with Q/T^2 etc. all disappear. Hence, as $S_{T=\infty}$ will evidently be of the form $3R \log \frac{T_\infty}{\tau} + S_a$, in which τ represents a constant temperature to be defined later, and S_a a possible additional constant:

$$S = 3R \left(\log \frac{T}{T_\infty} + \frac{1}{2} \frac{B}{T^2} + \frac{2}{3} \frac{C}{T^3} \dots \right) + R \log \frac{v-b}{v_{00}-b_{00}} + \left(3R \log \frac{T_\infty}{\tau} + S_a \right),$$

i.e.

$$S = 3R \log \frac{T}{\tau} + 3R \left(\frac{1}{2} \frac{B}{T^2} + \frac{2}{3} \frac{C}{T^3} \dots \right) + R \log \frac{v-b}{\omega} + S_a, \quad (a)$$

in which ω is the exceedingly small elementary volume $v_{00}-b_{00}$, which does not become $=0$ (even at the absolute zero there is always left the small space of the zero-point paths round the states of equilibrium), but remains $=(b_{00}+\omega)-b_{00}=\omega$.

In order to get a closer indication about the nature of the constants τ and S_a , we take, instead of the function of DEBIJE for E_t , which in general cannot be integrated (i.e. the part of E that bears relation to the temperature, hence outside the potential Energy), the simpler PLANCK-EINSTEIN function $E_t=E_0+3RT \frac{x}{e^x-1}=E_0+\frac{3R\theta}{e^x-1}$, which can be

integrated; in which now in $x=\frac{\theta}{T}$ the characteristic temperature $\theta=\beta v$

is a constant, independent of T and v . Then we get $c_v=\left(\frac{dE}{dT}\right)_v=$

$=3R \frac{x^2 e^x}{(e^x-1)^2}$, because $\frac{dx}{dT}=-\frac{\theta}{T^2}=-\frac{x}{T}$. Consequently, as x becomes

$=\infty$ for $T=0$, and $\frac{dT}{T}$ is $=-\frac{dx}{x}$:

$$\int_0^T \frac{c_v}{T} dT = - \int_\infty^x \frac{c_v}{x} dx = -3R \int_\infty^x \frac{x e^x}{(e^x-1)^2} dx = 3R \left[\frac{x e^x}{e^x-1} - \log(e^x-1) \right]_\infty^x,$$

i.e.

$$\int_0^T \frac{c_v}{T} dT = 3R \left[\frac{x e^x}{e^x-1} - \log(e^x-1) \right],$$

because $[\]$ becomes $=x-x=0$ for $x=\infty$. We may, therefore, also write:

$$\int_0^T \frac{c_v}{T} dT = 3R \left[\frac{x e^x}{e^x-1} - \log \frac{e^x-1}{x} \right] - 3R \log x,$$

so that finally (see above, as regards the term with v):

$$S = 3R \left[\frac{xe^x}{e^x - 1} - \log \frac{e^x - 1}{x} \right] + 3R \log x \frac{T}{\theta} + R \log \frac{v-b}{\omega}, \quad (b)$$

as $S_{T=0}$ is again $= 0$ (see § 1).¹⁾ This would therefore represent the quite general value of S , if the PLANCK-EINSTEIN function were valid. At low temperatures this is certainly not the case, but at high temperatures the DEBIJE function almost coincides with that of PLANCK-EINSTEIN, and when, therefore, we determine S at *higher* temperatures (in any case *small* values of x) from (b), we shall obtain the right expression. Then we find ($x=0$):

$$S = 3R + 3R \log \frac{T}{\theta} + R \log \frac{v-b}{\omega} \quad (x \text{ small}), \quad (c)$$

because the expression between [] becomes $= \frac{x(1+x)}{x + \frac{1}{2}x^2} - \log \frac{x + \frac{1}{2}x^2}{x} = (1 + \frac{1}{2}x) - \frac{1}{2}x = 1$.

Comparing (c) with (a) we accordingly see that the quantity τ introduced there is nothing but θ , for which in the DEBIJE theory of course its constant limiting value θ_0 at $T=0$, $v=v_0$ must be substituted, the constant S_a appearing to be $= 3R$. We may, therefore, finally write:

$$S = 3R \log \frac{T}{\theta_0} + 3R \left(\frac{1}{2} \frac{B}{T^2} \dots \right) + 3R + R \log \frac{v-b}{\omega} \left(\begin{matrix} RT\text{-region} \\ x_m \text{ small} \end{matrix} \right), \quad (11)$$

in which now everything is determined, for also ω (see below § 3) can be easily calculated. The quantities B, C , etc. are the volume functions in the Energy equation (3), which we can determine by means of the equation of state (see preceding Paper).

For ideal gases $v=\infty$ or very great; then B, C , etc. are $= 0$, and we get, substituting $\frac{1}{2}R$ for R in the temperature part:

$$S = \frac{3}{2}R \log \frac{T}{\theta_0} + \frac{3}{2}R + R \log \frac{v-b}{\omega} \quad (\text{ideal gases}), \quad (11^a)$$

in which v may now also be written for $v-b$.

¹⁾ As we have used the general function, valid for *all* values of T and v , we have, purposely, chosen the lower limits, so that $S_{T=0}$ occurs, of which we *know* that it is

$= 0$. Now the quantity $\left(\frac{dp}{dt} \right)_v$ under the second integral sign must, however, be taken at $T=0$. But we have already seen in I, § 2, that on assumption of the PLANCK-EINSTEIN function $\left(\frac{dp}{dt} \right)_v$ is always $= \frac{RT}{v-b}$, without additional degeneration-terms (hence $P=Q=S=$ etc. $= 0$).

Now by an entirely different way the following form has been found for mon-atomic gases (LORENTZ, PLANCK, TETRODE, and many others):

$$S = \frac{3}{2} R \log T + R \log (v-b) + \left[\frac{3}{2} R + R - R \log R + R \log \frac{k^{5/2} (2\pi m)^{3/2}}{h^3} \right],$$

which we may also write in the more homogeneous form:

$$S = \frac{3}{2} R \log \frac{T}{\theta_0} + \frac{3}{2} R + R \log (v-b) + R \log \frac{e k^{3/2} \theta_0^{3/2} (2\pi m)^{3/2}}{N h^3},$$

for $R = R \log e$ and $-R \log R = -R \log Nk$. This is, therefore, in perfect harmony with (11^a), if only we assume for the elementary volume $\omega = v_{00} - b_{00}$:

$$\omega = \frac{N}{e} \frac{h^3}{(k\theta_0)^{3/2} (2\pi m)^{3/2}} \dots \dots \dots (12)$$

That this really represents a *volume*, is easy to see. For the dimensions of the different quantities are $h = \text{erg. sec.}$, $k = \text{erg.} : T$, hence $k\theta_0 = \text{erg.}$, so that the dimensions of ω will be (N is the number of molecules in a Gr. mol.):

$$\frac{\text{erg}^{3/2} \text{sec}^3}{m^{3/2}} = \left(\frac{\text{erg}^{1/2} \text{sec}}{m^{1/2}} \right)^3 = \left[\left(\frac{m l^2}{t^2} \right)^{1/2} t : m^{1/2} \right]^3 = l^3.$$

3. Calculation of ω from the cyclic movement round the states of equilibrium in connection with the zero-point energy.

That the elementary volume ω — which will, of course, be the same, for all states of aggregation — is really equal to the above expression (with a difference of a numerical factor, which is near 1), so that we might have immediately written this value for it, even without statistic and other considerations — and through which the Entropy-constant would come into our possession without any difficulty — may appear from what follows.

In the neighbourhood of the absolute zero the molecule centres in solid substances (which we choose for convenience sake) will still describe paths with exceedingly small distances round the positions of equilibrium in consequence of the periodically acting attractive and repulsive forces ¹⁾.

The vis viva of this movement is $2 \times \frac{1}{2} mu^2$, when u is the velocity with which the path is passed through. Now $u = 2\pi r\nu$, when ν represents the number of revolutions per second, which quantity is evidently identical with the frequency ν of the elastic waves introduced by DEBYE, the quasi-linear vibrations of which may be considered as projections of the said revolutions round the positions of equilibrium on the path-diameters ($= 2r$). Thus we have:

$$4\pi^2 r^2 m \nu^2 = \frac{9}{8} k\theta_0 + aT^4 \dots,$$

¹⁾ Cf. also These Proceedings 21, 1184 (1919), 23, 887 (1920) and especially These Proceedings 24, 294 (1921).

as the zero-point energy according to DEBYE is $= \frac{9}{8} R \theta_0 : N = \frac{9}{8} k \theta_0$ for one molecule. The terms with aT^4 , etc. ($a = A : N$, etc.) remain, so long as T has not yet become $= 0$. (In this the coefficients a etc. are still functions of v). As further $\beta v = \theta$, we may write — now passing to the limit $T = 0$:

$$4\pi^2 r_0^2 m \frac{\theta_0^2}{\beta^2} = \frac{9}{8} k \theta_0.$$

i.e.

$$r_0^2 = \frac{9}{32\pi^2} \frac{k \beta^2}{m \theta_0} = \frac{9}{32\pi^2} \frac{h^2}{k m \theta_0} = \frac{9}{16\pi} \frac{h^2}{k \theta_0 \cdot 2\pi m},$$

because $\beta = h : k$. (Accordingly the quantity h appears here for the first time in consequence of the equation $\theta = \beta v$). The volume of the space thought spherical, which the molecule centres thus leave in their circular paths (in all possible planes) round the positions of equilibrium, will be $= \frac{4}{3} \pi r_0^3$, so that for the limiting space indicated above by $\omega = v_{00} - b_{00}$ (ω refers to 1 Gr. mol. $= N$ molecules) we get:

$$\omega = N \times \frac{4}{3} \pi \left(\frac{9}{16\pi} \right)^{3/2} \left(\frac{h^2}{k \theta_0 \cdot 2\pi m} \right)^{3/2},$$

i.e.

$$\omega = \frac{9}{16} \frac{N}{\sqrt{\pi}} \frac{h^3}{(k \theta_0)^{3/2} (2\pi m)^{3/2}}, \quad \dots \quad (12^a)$$

which in fact — except for a numerical factor — is in harmony with the value (12) found in an entirely different way¹⁾. Instead of $\frac{1}{e} = \frac{1}{2.72}$ there stands $\frac{9}{16\sqrt{\pi}}$ as fore-factor, i.e. $\frac{1}{1.78 \times 1.77} = \frac{1}{3.15}$, which is 1.16 times smaller. But this does not greatly affect the matter itself in my opinion, seeing that there is no absolute agreement in the statistic theory either, concerning the numerical factors which occur in the proportionality of ω to h^3 . Our considerations form a bridge, so to say, between the Entropy constant and the theory of the cyclic movements in the sense of HELMHOLTZ.

In conclusion we may still remark that our equations (11) and (11^a) are now also perfectly homogeneous: S has the dimensions of R . Under the log sign there stands, below T , duly another (constant) temperature θ_0 ; below $v - b$ another (constant) volume ω .

¹⁾ This derivation was already found by me many years ago, and is inserted in my book on the thermodynamic functions of simple substances and of mixtures with a number of new things. But for various reasons the completion of it has been much delayed, so that I avail myself of this opportunity to make these considerations public, which, I believe, are new.

As appears from the derivation, (11) holds of course only for the RT -region. Hence for gases (see fig. 1) $T=0$ and $v \rightarrow v_{00}$ can never occur simultaneously, but $T=0$ and $v=\infty$ (at very low temperatures), or $T=\infty$ (great) and v arbitrary (in the so-called fluid region). For the T^4 -region, which occurs only for solid substances (Fig. 1, left of B), formula (10) of § 1 is valid, and this gives $S=0$ at $T=0$. But for gases S can never become $=0$. Here follow some limiting values.

a) $T=0, v=\infty$ (Fig. 1, at O): $S=\frac{3}{2} \log 0 + R \log \infty = \infty$,

as v then varies $\propto e^{1/T}$ (on the saturation line), or (below it) in a still greater degree, so that $\log v$ becomes $\propto \frac{1}{T}$. The first term of S ($\propto \log T$) will accordingly be very small with regard to the second term, which is $\propto \frac{1}{T}$. Hence the volume is predominant.

b) $T=\infty, v=\infty$ (Fig. 1 on the T -axis, quite on the right):

$$S=\infty + \infty = \infty.$$

c) $T=\infty, v=\omega$ (Fig. 1 quite on the right above at $p=\infty$):

$$S=\infty + 0 = \infty.$$

Just as in Chapter I for E we give in conclusion the following summary for S ¹⁾.

$$\left\{ \begin{array}{l} S = 3R \log \frac{T}{\theta_0} + 3R \left(\frac{1}{2} \frac{B}{T^2} \dots \right) + 3R + R \log \frac{v-b}{\omega} \quad (x_m \text{ small: } RT\text{-region}). \\ \left\{ \begin{array}{l} S = 3R \left[\frac{x e^x}{e^x - 1} - \log \frac{e^x - 1}{x} \right] + 3R \log \frac{T}{\theta} + R \log \frac{v-b}{\omega} \quad (\text{in general, according to PLANCK-EINSTEIN}). \\ S = \int_0^T \frac{c_v}{T} dT + \int_{v_{00}}^v \left(\frac{dp}{dt} \right)_v dv \quad (\text{in general, according to thermodynamics}). \end{array} \right. \\ S = \frac{4}{3} A T^3 + \frac{8}{7} B T^4 \dots \quad (\text{according to DEBIJE}) \quad (x_m \text{ great: } T^4\text{-region}). \end{array} \right.$$

¹⁾ It is self-evident that for the temperature part of S in general $3R$ must be replaced by c , when by c is represented the specific heat at constant infinitely great volume. For mon-atomic solid substances c is then $3R$, for multi-atomic substances $>3R$; for mon-atomic gases $c=3/2 R$, for multi-atomic gases $>3/2 R$; etc. The R before $\log \frac{v-b}{\omega}$ always remains R , because it results from the RT of the equation of state and only the progressive Energy plays a part here, but ω is modified. It is further noteworthy that for convenience we have always put here $\log (v-b)$ for $\int \frac{dv}{v-b}$, neglecting the volume variability of b . If this is taken into account, the term with $\log (v-b)$ becomes somewhat more intricate. (See the note concerning $\int \frac{\lambda}{v-b} dv$ in § 2 of Chapter II of our foregoing Paper).

And now we have completed our considerations on Entropy and the Entropy-constant, and in a fourth (concluding) Paper we can draw up the *vapour-pressure equations*, both for the equilibrium liquid-vapour and for solid-vapour, the latter up to the absolute zero-point — making use of the expressions for E found now (required for the calculation of the melting-point and evaporation heats) and for S (required for the vapour pressure constants). At the same time the question concerning the so-called “zero-point vapour pressure” will then be discussed.

Tavel sur Clarens, 1926.

Chemistry. — "*Equilibria in systems, in which phases, separated by a semipermeable membrane*". XV. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 27, 1926).

Ternary systems in which dimixtion into two and three liquids occurs.

We now shall consider the case that also three liquids can be in equilibrium with one another. In the figures 1 and 2 in which only the angle-point W of the components-triangle is drawn, q_1 q_2 and q_3 represent the three liquids being in equilibrium with one another. As each point within the triangle q_1 q_2 q_3 represents a complex of those three liquids, we may call therefore, triangle q_1 q_2 q_3 also the region of dimixtion of three liquids.

At each side of triangle q_1 q_2 q_3 joins a region of dimixtion of two liquids; consequently there are three of those regions of dimixtion and also, therefore, three binodalcurves. In fig. 1 on the binodalcurve q_1 α q_2 a critical liquid α is drawn.

The branches of the binodalcurves are drawn in the figures, as if they terminate in the points q_1 q_2 and q_3 ; this is, however, not the case, they continue viz. within the region of dimixtion¹⁾. If we limit ourselves to stable states, then we may leave out of consideration those parts, situated within the region of dimixtion, which represent only metastable and unstable states.

For the position of two binodalcurves in the vicinity of their point of intersection is true:

both curves are situated either both within the conjugation-angle or both within the supplement-angle; if the one curve touches the one leg, then the other curve touches the other leg.

As liquid q_1 can be in equilibrium with the liquids q_2 and q_3 , angle q_2 q_1 q_3 (and its opposite angle) is the conjugation-angle in point q_1 . The two binodalcurves are drawn in the vicinity of q_1 (figs 1 and 3) within the supplement-angle; this is also the case in the other points q_2 and q_3 of those figures, excepted in the point q_3 of fig. 2 in which both curves are situated within the conjugation-angle q_1 q_2 q_3 .

In the previous communication we have deduced:

¹⁾ For considerations more in detail compare: F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. Drittes Heft; Zweiter Teil, pg. 297 and following, figs. 120—124.

the O.W.A. of the liquids of a binodalcurve increases in that direction in which we move away from the point W along this curve.

If we apply this rule to the binodalcurve $q_1 a q_2$ (fig. 1), then follows that the O.W.A. of the liquids must increase starting from a towards

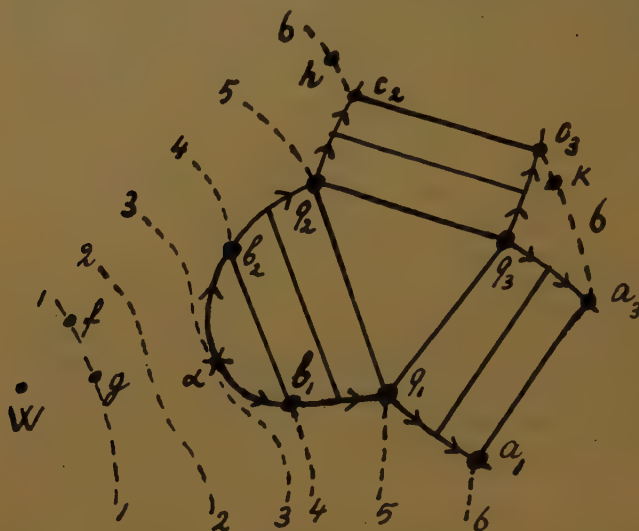


Fig. 1.

q_1 and q_2 , consequently in the direction of the arrows; it follows for the branches $q_2 c_2$ and $q_3 c_3$ that the O.W.A. increases starting from q_2 towards c_2 and starting from q_3 towards c_3 and for the branches $q_3 a_3$ and $q_1 a_1$ starting from q_3 and q_1 towards a_3 and a_1 . If we apply this rule also to the binodalcurves of fig.

2, then we see that the arrows in both figures indicate the direction in which the O.W.A. increases along the binodalcurve.

The dotted curves of those figures represent isotonic curves; they are only drawn so far as they represent stable states and are situated, therefore, out of the region of dimixtion. In the previous communications we have discussed already the parts of those curves situated within the region of dimixtion and we have also deduced the conditions which must be satisfied by binodalcurves and isotonic curves in the vicinity of their point of intersection.

Let us firstly consider fig. 1. The isotonic curve 3, which touches the binodalcurve in the critical point a , is curved in this point in the same direction as the binodalcurve; the isotonic curve 4 consists of two branches, which are united with one another by the conjugationline $b_1 b_2$. As the liquids q_1, q_2 and q_3 can be in equilibrium with one another and have, therefore, also the same O.W.A., the isotonic curve 5 consists still also of the isolated point q_3 besides of the two branches, which are united by the conjugationline $q_1 q_2$. Consequently all liquids of curve (5) have the same O.W.A. as liquid q_3 . If we represent an arbitrary liquid of curve 5 by L_5 , then we can have, therefore, the osmotic equilibrium:

$$L_5 | L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. 1.}$$

Of course herewith it is immaterial which is the ratio of the quantities of the liquids at the right side of the membrane and whether one or two of those are totally failing.

The isotonic curve 6 consists of three branches, which are united with one another by the conjugation-lines $c_2 c_3$ and $a_1 a_3$. If we represent a liquid of curve 6 by L_6 , we can have a.o. the following osmotic equilibria:

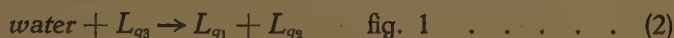


Of the many phenomena, which may occur in osmotic systems, we only shall discuss a few of them.

Let us take the osmotic system:



in which L represents a liquid, which is situated at the same side of curve 5 and the line $q_1 q_2$ as point W . As, therefore, the O.W.A. of the system at the right side of the membrane is larger than that of the liquid L , the water in (1) diffuses, therefore, from left towards right, as is indicated by the arrow. Consequently, in the system at the right side of the membrane, as appears at once from fig. 1, the reaction:



occurs, so that the quantity of the liquids q_1 and q_2 increases, but that of q_3 decreases. We now assume that so much of the liquid q_3 is present, that the system at the right side of the membrane remains. Then it depends on the composition of liquid L , which osmotic equilibrium will be formed from (1). If we take f.i. the liquid f then (1) passes into:



in which L'_f is the point of intersection of the line Wf with the isotonic curve (5). If we take in (1) for L f.i. the liquid g or the critical liquid α or a complex of the liquids b_1 and b_2 , then is formed at the left side of the membrane the same system as at the right side, or the system $L_{q_1} + L_{q_2}$.

We now take a liquid L which is situated at the other side of curve 5 and the lines $q_1 q_3$ and $q_2 q_3$ than point W . As the O.W.A. of this liquid is greater now than that of the complex of the three liquids, we now have, therefore, an osmotic system:



in which water diffuses from right to left. At the right side of the membrane then occurs the reaction:



so that the quantity of liquid q_3 increases, and that of q_1 and q_2 decreases. We now assume that there is present so much of the liquids q_1 and q_2 , that the system at the right side of the membrane remains. If we take in (4) for L f.i. the liquid L_h , then is formed the osmotic equilibrium:



in which L_h^1 is represented by the point of intersection of the line Wh with curve 5. If we take in (4) for L the liquid K then is formed at the left side of the membrane the same system as at the right side or the system $L_{q_2} + L_{q_3}$.

Let us take once more the osmotic system:

$$L_f \xrightarrow{\quad} L_{q_1} + L_{q_2} + L_{q_3} \quad \text{fig. 1} \dots \dots \dots (7)$$

in which the water diffuses in the direction of the arrow, so that at the right side of the membrane reaction (2) takes place. If no sufficient quantity of the liquid q_3 is present, so that this disappears totally, then it depends on the ratio of the quantities of the liquids which osmotic equilibrium will be formed. We imagine the complex of the three liquids at the right side of the membrane to be represented by a point Q (not drawn) which is situated anywhere within the triangle $q_1 q_2 q_3$. The complex of the total system (7) is represented then by a point R (not drawn) which is situated anywhere on the line fQ . The position of the point R now defines on which isotonic curve the osmotic equilibrium which must arise from (7) will be formed. If this is the case f.i. on the isotonic curve (2) then arises the osmotic equilibrium:

$$L_f' \mid L_Q'$$

in which L_f' and L_Q' represent the points of intersection of the lines Wf and WQ with curve 2. If the equilibrium is formed on the isotonic curve 3, then L_f' and L_Q' represent the points of intersection of the lines Wf and WQ with curve 3. If it is formed on the isotonic curve 4, then may arise the osmotic equilibrium

$$L_f' \mid L_{b_1} + L_{b_2} \quad \text{fig. 1}$$

in which L_f' is the point of intersection of the line Wf with curve 4. The ratio of the quantities of both liquids at the right side of the membrane is defined by the point of intersection of the lines WQ and $q_1 q_2$.

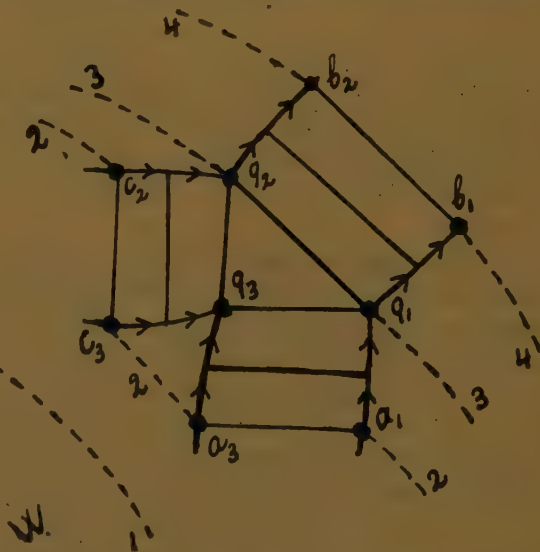
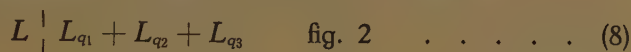


Fig. 2.

We now take fig. 2. The isotonic curve 2 consists of three branches, which are united by the conjugation-lines $a_1 a_3$ and $c_2 c_3$; the isotonic curve 3 consists, besides of two branches, which are united with one

another by the conjugation-line $q_1 q_2$, still also of the isolated point q_3 ; the isotonic curve 4 consists of the two branches, united by the conjugation-line $q_1 q_2$.

We now consider the osmotic system:



If herein L represents a liquid or a complex of two liquids, which is situated on the same side of curve 3 and the lines $q_1 q_3$ and $q_2 q_3$ as the point W , then L has a smaller O.W.A. than the system of the three liquids. In (8) water diffuses, therefore, from left to right. It appears from fig. 2 that then at the right side of the membrane the reaction:



occurs. If L is situated in (8) at the other side of curve 3 and the line $q_1 q_2$ than the point W , then the water in (8) diffuses from right to left. Then at the right side of the membrane the reaction:



occurs. The reader now can easily deduce the osmotic equilibria, which may be formed from system (8) and other osmotic systems of fig. 2.

If we compare the figs 1 and 2 with one another, then we see that in both three regions of dimixtion of two liquids join at the region of dimixtion $q_1 q_2 q_3$ of three liquids.

Starting from the region of dimixtion of the three liquids in fig. 1 the O.W.A. increases along two of the binodalcurves and it decreases along the third, in fig. 2, however, the O.W.A. decreases along two of the binodalcurves and it increases along the third.

One could still imagine two other cases viz. that the O.W.A. either increases or decreases along each of the three binodalcurves; this is impossible, however. If we consider viz. the position of point W and of triangle $q_1 q_2 q_3$ with respect to one another, then we find only the two cases, represented by figs 1 and 2. As long as we assume viz. that the diffusing substance W is a component, point W cannot be situated within the triangle $q_1 q_2 q_3$. We shall refer to this later.

The change of the O.W.A. of the liquids of a saturation-curve of a solid substance.

In the communications III and IV we have deduced a rule for the change of the O.W.A. of the liquids of a saturation-curve. We found that the O.W.A. in the figs 1, 2 and 3 (Comm. III) in which wv represents the saturation-curve of the solid component Y , increases in the direction of the arrows viz. from w towards v . The same is true for curve wv which represents in fig. 1 IV the saturation-curve of a hydrate H and for curve wv , which represents in fig 2 IV the saturation-curve of a ternary compound F . If the diffusing substance is

another than water, as f. i. the component Y in the figures of the communication XI and XII, then a corresponding rule is valid.

In fig. 3 (of this communication) a q_1 and $q_1 f$ represent two parts of the saturation-curve of the substance F . This curve intersects the binodal-curve $q_1 \alpha q_2$ in the two conjugated points q_1 and q_2 so that also an equilibrium:

$$F + L_{q_1} + L_{q_2} \quad \text{fig. 3}$$

can exist. Of course the saturation-curve does not finish in q_1 and q_2 , but it passes through the region of dimixtion. If the saturation- and the binodal-curve intersect one another only in two points, then it goes, as is indicated in the figure by the dotted curve $q_1 m n q_2$, from q_1 towards q_2 ¹⁾. This part, situated within the region of dimixtion represents only metastable and unstable states.

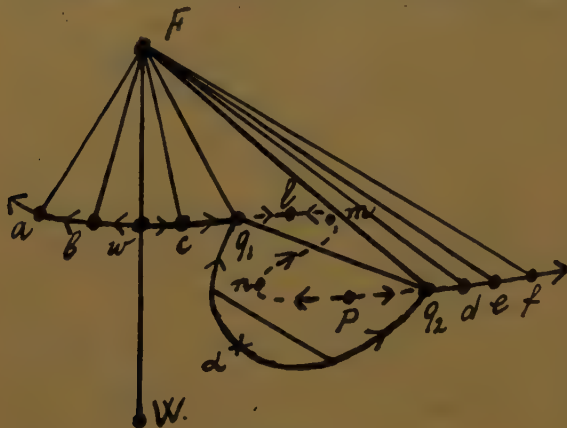


Figure 3.

fore, from w towards a and towards q_1 and from q_2 towards f . As q_1 and q_2 are conjugated liquids and have, therefore, the same O.W.A., it appears, also from this at once that the rule above-mentioned cannot be valid for the part $q_1 m n q_2$. In order to examine this more in detail, we represent the composition of an arbitrary liquid L by:

$$x \text{ quant. } W + y \text{ quant. } F + (1-x-y) \text{ quant. } N \quad . \quad . \quad . \quad (11)$$

in which N is an arbitrary liquid of the saturation-curve. It is clear, however, that we are not allowed to take for N the liquid w or a liquid in the immediate vicinity. Consequently we have a system of coordinates with the point N as origin, the line NW as X -axis and NF as Y -axis.

If the liquid L defined by (11) is saturated with the solid substance F , then is satisfied:

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} = \zeta_F \quad . \quad . \quad . \quad (12)$$

¹⁾ For the case there are more points of intersection, compare F. A. H. SCHREINEMAKERS l.c., figs. 136—139. Examples of similar diagrams are found in the system: water + phenol + anilin.

while the *O.W.A.* of this liquid is defined by:

$$\varphi = \zeta + (1-x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \quad . \quad . \quad . \quad (13)$$

With the aid of (12) we can also write for this:

$$\varphi = \frac{\partial \zeta}{\partial x} - \frac{\partial \zeta}{\partial y} + \zeta_F \quad . \quad . \quad . \quad (14)$$

For a liquid; which differs infinitely little from *L*, are valid, therefore:

$$[-xr + (1-y)s] dx + [-xs + (1-y)t] dy + A = 0 \quad . \quad . \quad (15)$$

$$\Delta\varphi = (r-s) dx + (s-t) dy + B \quad . \quad . \quad . \quad (16)$$

in which *A* and *B* contain terms of higher order. If liquid *L* coincides with the point *N*, so that $x=0$ and $y=0$, then they pass into:

$$s dx + t dy + A_0 = 0 \quad . \quad . \quad . \quad (17)$$

$$\Delta\varphi = (r-s) dx + (s-t) dy + B_0 \quad . \quad . \quad . \quad (18)$$

so that we may write for (18) also

$$\Delta\varphi = r dx + s dy + A_0 + B_0 \quad . \quad . \quad . \quad (19)$$

Limiting ourselves to magnitudes of the first order, then follows from (17) and (19):

$$\frac{dy}{dx} = -\frac{s}{t} \quad . \quad . \quad . \quad (20^a) \quad \Delta\varphi = \frac{rt-s^2}{t} dx \quad . \quad . \quad . \quad (20^b)$$

The equations (17) and (19) and consequently also (20^a) and (20^b) define the direction of the saturation-curve and the change of the *O.W.A.* in each arbitrary point (excepted in the vicinity of the point *w*).

We now take an arbitrary point of the saturation-curve outside the region of dimixtion f. i. the point *b*. As *t* is positive in this point, $s:t$ can never be infinitely large, therefore; it now follows from (20^a) that the saturation-curve in *b* cannot touch the *Y*-axis, viz. the line *bF*.

If we take dx positive, then we go along the curve from *b* towards *w*; if we take dx negative, then we go from *b* towards *a*. As the coefficient of dx in (20^b) is positive, it follows that φ decreases starting from *b* towards *a*, so that the *O.W.A.* increases from *b* to *a*. If we apply this same to other points of the saturation-curve situated outside the region of dimixtion, then we see that the *O.W.A.* increases in the direction of the arrows, viz. in that direction, in which we move away from the point *w* along the saturation-curve.

If we go along the saturation-curve from q_1 towards q_2 then we intersect the spinodal-curve in the two points *l* and *p*, in which, therefore, $rt-s^2=0$. In accordance with (20^a) the saturation-curve shows nothing particular in those points. In accordance with (20^b) the change of the *O.W.A.* is zero in those points, however, and the *O.W.A.* itself a maximum or minimum, therefore.

It follows for B :

$$B = \frac{1}{2} \left(\frac{\partial r}{\partial x} - \frac{\partial s}{\partial x} \right) dx^2 + \left(\frac{\partial r}{\partial y} - \frac{\partial s}{\partial y} \right) dx dy + \frac{1}{2} \left(\frac{\partial s}{\partial y} - \frac{\partial t}{\partial y} \right) dy^2$$

so that (22) passes into:

$$(1-y) \Delta \varphi = \left(\frac{1}{2} r dx^2 + s dx dy + \frac{1}{2} t dy^2 \right) (23)$$

If the point w is situated out of the region of dimixtion, the second part of (23) is always negative. If, as in fig. 3, the point w is situated between W and F then $1-y$ is positive. Consequently $\Delta \varphi$ is negative, φ is a maximum, therefore, and the *O.W.A.* in w a minimum. If w is situated at the other side of point F as f.i. point v in fig. 2 IV, then $1-y$ is negative; the *O.W.A.* is then a maximum in this point.

(To be continued).

Palaeontology. — "*Some further remarks concerning tertiary fish-otoliths from the Netherlands.*" By O. POSTHUMUS. (Communicated by Prof. J. F. VAN BEMMELEN.)

(Communicated at the meeting of March 27, 1926)

Some time ago I received for study from the Netherlands Geological Survey ('s Rijks Geologische Dienst) a collection of otoliths, which had been found in some test-borings in the Southern and South-western part of the Netherlands. On this material the following remarks are based.

Concerning the determinations the same may be said as on a former occasion¹⁾. It seems to me that a more thorough study of fossil fish-otoliths is only possible, when we have more data about those of recent fishes. Only then can we get a clearer idea as to the relative value of the different characteristics observed. It is to be hoped that the investigations which have been begun by G. ALLAN FROST²⁾, may be continued on a sufficiently large scale to afford a solid basis for comparison in the future.

From Miocenic strata otoliths occur in the following borings³⁾:

Boring Reek (handboring 48, Jaarverslag Rijksopsporing van Delfstoffen over 1909, p. 21). Here, at a depth of from 140 to 157 M., in strata of Mid Miocene age, the following forms occurred:

Otolithus (*Gadus*) *elegans* Koken (O. M. P.); this form is the most frequent; some of them may be taken as belonging to the variety *sculpta*.

O. (*Merluccius*) *emarginatus* Koken (O. M.).

O. (*Merlangus*) *cognatus* Koken (O. M.).

O. (*Raniceps*) *latisulcatus* Koken (O.).

O. (*Ophidiidarum*) *difformis* Koken (O. M.); some of the specimens belong to the variety *acutangulus*.

O. (*Scopelus*) *austriacus* Schubert (M.).

O. (*Macrurus*) *Toulai* Schubert (M.).

O. (*Macrurus*) *pusillus* O. Posth. (M.).

As may be seen from the additional indications, O. (*Raniceps*) *latisulcatus* in other localities occurs in the Oligocene only; O. (*Macrurus*) *Toulai* and O. (M.) *pusillus* in the Miocene only; O. (*Scopelus*) *austriacus* occurs in the Pliocene of Sardinia too, but in a somewhat

¹⁾ O. POSTHUMUS, Verhand. Geol. Mijnbouwk. Gen. voor Nederl., VII, 1923, p. 107; O. POSTHUMUS, Otolithi piscium, Fossilium Catalogus, pars 24, 1924, p. 3; in the latter further literature can be found.

²⁾ Annals and Mag. Nat. Hist., vol. XVI, 1925, p. 433-446.

³⁾ After the names I have indicated the period in which the otoliths have been found in other localities: O = Oligocene, M = Miocene, P = Pliocene.

different form. The other species occur both in the Oligocene and the Miocene.

Boring Bakel (handboring 52, Hazenhut, Jaarverslag 1909, p. 23).

Here, at a depth of from 56 to 66 M., in Upper Miocenic strata the following forms were found :

O. (*Gadus*) *elegans* Koken (O. M. P.); this is also here the most frequent species; some specimens belong to the variety *sculpta*.

O. (*Merluccius*) *emarginatus* Koken (O. M.).

O. (*Fierasfer*) *nuntius* Koken (O. M.).

O. (*Solea*) *subglaber* Schubert (M.).

O. (*Serranus*) *Noetlingi* Koken (O. M.).

O. (*Box*) *insignis* Prochazka (M.).

A number of Macruridae were also found, some of them closely resemble species previously described by me. It seems to me, however, that it is better to postpone a further discussion of these species until we have a better knowledge of the limit of variation in recent allied forms.

In this locality many of the forms are also known from Oligocene strata.

In Pliocenic strata the following species have been found :

In test-boring Beers (boring 58, Jaarverslag 1909, p. 24) in strata of Mid-Pliocenic age, at a depth of from 40 to 74.50 M. :

O. (*Gadus*) *merlangus* Newton (P.).

O. (*Gadus*) *luscus* Newton (P.).

O. (*Macrurus*) aff. *Toulai* Schub.

In test-boring Zeeland II (boring 66, Jaarverslag 1910, p. 22) from strata of Mid Pliocenic age, at a depth of from 22.50 to 60 M. :

O. (*Gadus*) *merlangus* Newton (P.).

In these borings the marine Upper Pliocene does not occur; in the Maassluis test-boring at a depth of from 161.40 to 168.40 M., these strata were, however, found and

O. (*Gadus*) *merlangus* Newton (P.) occurred there.

In the test-boring Sommelsdijk some otoliths were found in strata from 67.80 to 68.50 M., which, according to the opinion of Dr. STEENHUIS, are younger than the above mentioned strata of Maassluis. The otoliths are practically identical with those of the cod and haddock; this bears out the above mentioned supposition.

When studying this material, I was again struck by the fact, that the difference between the fishfauna of the Oligocene and Miocene in these regions is but slightly pronounced. Many forms, which were at first known from one period only, have afterwards been found in the other one as well. It seems, however, that in these countries the fauna of the Oligocene and Miocene on the one hand and that of the Eocene on the other hand, which is known to us from the researches of Priem, Schubert and Leriche from France, England and Belgium, differ far more widely.

Although in the Pliocene the otoliths are also sometimes rather numerous, they belong in these regions to a few species only, which closely resemble

living forms, such as *Gadus luscus* and *Gadus merlangus*. Only a few species from the Miocene occur, in slightly altered forms, in the Pliocene too.

It is not possible, to form an opinion as to what circumstances this is due to; whether it is due to the extinction of the species or to their migration e.g. in connection with alterations of the climate or to other causes.

I wish to conclude by expressing my hearty thanks to Dr. STEENHUIS, Geologist to the Geological Survey, who kindly placed the material at my disposal and provided some data.

Physics. — “A yellow green discharge in potassiumvapour.” By T. L. DE BRUIN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 27, 1926)

Working with the electrodeless arrangement for investigation of the spectrum of ionised potassium¹⁾, it was found that two distinct types of discharges could be obtained. If the bulb a long time was heated and then the spark gap was diminished in length, the appearance of the bright blue ring with the spectrum of K. II changed abruptly to a faint diffuse discharge with an yellow green colour, filling almost the whole bulb. Photograph VI in the accompanying plate, made with a HILGER glassspectrograph, is a photograph of the “blue violet” discharge (exposure 3 minutes) and the “yellow green” discharge (exposure 3 hours). The “green” spectrum is very simple and showed the following lines of the first and second subordinate series of the arc spectrum.

II. Subordinate series.

6939.5	$2p_1-3s$
6911.8	$2p_2-3s$
5802.0	$2p_1-4s$
5782.7	$2p_2-4s$
5340.1	$2p_1-5s$
5323.5	$2p_2-5s$
5099.6	$2p_1-6s$
5084.5	$2p_2-6s$
4956.8	$2p_1-7s$
4943.1	$2p_2-7s$

I. Subordinate series.

5832.2	$2p_1-5d$
5812.5	$2p_2-5d$
5339.9	$2p_1-6d$
5343.3	$2p_2-6d$
5112.7	$2p_1-7d$
5097.7	$2p_2-7d$
4965.5	$2p_1-8d$
4952.2	$2p_2-8d$

The “forbidden” line $1s-d_{12}$, 4642 \AA was faintly visible. The *D* lines of sodium were also present. It was at first thought, from the plates, that these lines here have an abnormal ratio in intensity, but the photograph showed the ratio $1:2^2$).

It is interesting to note that in this type of discharge the strong lines of the arcspectrum λ 4047 and 4044, members of the chief series, very faintly made their appearance. It is probably not only due to the glassabsorption. It seems that LOCKYER³⁾ and FREDENHAGEN⁴⁾ have observed,

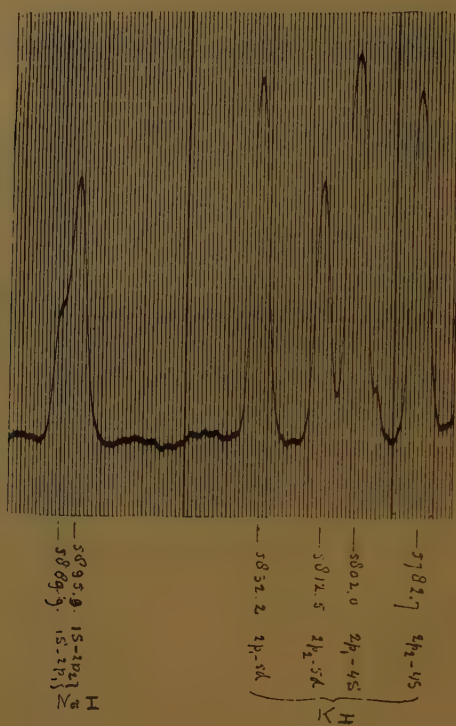
1) Following communication in these Proceedings: “The spectrum of ionised potassium.

2) The wavelenghts in the photogram must be changed.

3) N. LOCKYER: Proc. R. S. 29. 140. 1879.

4) FREDENHAGEN: Phys. Z.S. 1907. pg. 734.

though under other conditions, such an appearance, that mainly subordinate series are present.



Physics. — "*The spectrum of ionised potassium.*"¹⁾ (First communication).

By T. L. DE BRUIN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 27, 1926).

1. Introduction.

According to the theory of BOHR and SOMMERFELD, the arc spectrum originates from the neutral atom, whereas the spark spectrum of the 1st, 2nd, 3rd... order originates from the 1, 2, 3 times ionised atom. All series, having R for constant (RYDBERG constant) are produced by neutral atoms, while those, having $4R$, $9R$... for the constant, have their origin in the 1, 2, 3 times ionised atom. The "displacement law" of SOMMERFELD and KOSSEL²⁾ states that the spark spectrum of every element resembles in structure the arc spectrum of the element preceding it in the periodic system and that the spark spectrum of the 1st, 2nd, 3rd... order resembles the arc spectrum of the element 2, 3,... stages preceding it in the periodic system. These spark spectra of the multi-ionised atoms are of great interest in connection with the general structure of the atoms. By the work of FOWLER, PASCHEN, MILLIKAN and BOWEN a.o. the displacement law has been verified quantitatively. The multiplicity of the term system attained in any spectrum is in simple connection with the degree of ionisation of the atom.

2. The spark spectrum of potassium. Observational data.

The spark spectrum of potassium³⁾ has been the subject of numerous investigations of which a summary has been given in Table 1.

Little progress, however, has been made in the detection of regularity in the spectrum. The accuracy of different measures is not sufficient for a scrutinising analysis. Moreover the spectrum is very complex. ZEEMAN and DIK got a pure spectrum by means of the electrodeless discharge. From the preliminary observations, DIK and ZEEMAN concluded that in the spectrum constant differences of about $\Delta\nu = 847$ were present⁴⁾. In the Amsterdam Laboratory observations with a grating spectograph

1) Previous note: T. L. DE BRUIN and P. ZEEMAN, Nature. January 1925. No. 2882. This note deals with the probable existence of a quintetlevel in the spark spectrum of Potassium. Some examples of quintets are given. We have extended later these groups of 5 lines to groups of 9 lines. In the summer 1925 we communicated this classification to Prof. A. FOWLER F. R. S. Recently DAHMEN of Bonn has extended the quintetlevel with 9 new levels. Two of them coincide with our levels.

2) SOMMERFELD and KOSSEL: Verh. d. D. Phys. Ges. 21. 240. 1919.

3) KI indicates the arcspectrum, KII the first sparkspectrum, etc. It is not certain that the spectrum in question only originates from KII .

4) We have found this difference as: $P_3 - P_4 = 845.5$. It is however not of so fundamental significance as supposed initially.

TABLE I.

Author	Method, etc.	Spectral region	Literature	Remarks
1. EDER and VALENTA:	The metal in an hydrogenatmosphere. Vigorous condensed discharges. Besides the arc spectrum a new spectrum, very rich in lines.	λ 7700— „ 2200	Denkschr. Wien. Akad. 61, 347, 1894	
2. GOLDSTEIN:	Vigorous condensed discharges through powdered salts f. i. KCL. „Grund spectrum“. Arc lines absent.	16 lines	Verh. d. D. Phys. Ges. 9, 321, 1907 und 12, 246, 1914	
3. SCHILLINGER:	As 1. Grating- and quartz-spectrograph. Arc- and spark lines.	λ 7700— „ 2200 (ROWL)	Wien. Sitz. ber. 118, 2a, 605, 1909	
4. NELTHORPE:	As 2; another type of tube. Glass spectrograph. Arc lines absent.	λ 6307— „ 3898 (I. Å)	Astr. Journ. 41, 16, 1915	There are probably chlorine lines.
5. MC. LENNAN:	Electrodeless discharge. Quartz-spectrograph and vacuum grating.	λ 6590— „ 3489 (± 0.5 Å) „ 3346— „ 1873	Proc. R. S. London 100, 182, 1921	There are mercury lines.
6. FOOTE, MEGGERS and MOHLER:	Electrical measurements of critical potentials at ± 19 and ± 23 Volts. Quartz-spectrograph.	λ SCHILLINGER	Astr. Journ. 55, 145, 1922	
7. ZEEMAN and DIK:	Electrodeless discharge. Arc lines absent.	λ 7700— „ 2342 (± 0.2 Å)	Proc. R. S. Amsterdam, 1922, 1925 Ann. d. Phys. 71, 162, 1923	
8. ROBERTSON:	Electrodeless discharge. Glass spectrograph. Principally arc lines. A few spark lines.	λ 5007 „ 4831 „ 4607 „ 4505 „ 4390 „ 4314	Phys. Rev. Series XIX, 470, 1922	It seems that ROBERTSON not obtained the good discharge.

TABLE I (Continued).

Author	Method, etc.	Spectral region	Literature	Remarks
9. DAHMEN:	Potassium electrodes in argon. Arc- and sparklines. Grating.	λ 7000— „ 3400 (0.003 Å) (1. Å)	Zeitschr. f. Phys. 29, 1924	There are argonlines.
10. SHAVER:	Electrodeless discharge. Fluoritispectrograph.	λ 1896— „ 1602 (1. Å) (0.3 Å)	Trans. R. S. Canada Section III, 1924	
11. BOWEN and MILLIKAN:	„Hotspark“.	λ 312— „ 1303	Phys. Rev. 23, 1924	
12. MOHLER:	Excitations potentials \pm 19, 23 and 28 volts.	—	Sc. Papers. Bureau of Standards. Washington, N. 505, 1925	
13. KIMURA and NAKAMURA:	Cathodespectra. Method of long and short lines. „Enhanced“-lines of one kind, KII.	No data	Sc. Papers. Inst. Phys. a. Chem. Res. Tokyo, 1925.No. 30	

were projected for further investigation. Prof. KONEN kindly informed us that in Bonn such measurements were already in hand, so that they were here postponed; DAHMEN of Bonn has published recently measurements on ionised potassium. His measurements are very accurate and can be of service for a scrutinising analysis. It should be remarked that different lines given by DAHMEN have not been recorded by any other observer.¹⁾ We have investigated this question in connection with our termscheme and have extended the observations into the region of shorter wave lengths.

3. Apparatus.

For studying the spectrum again the electrodeless discharge was employed. A bulb of pyrexglas with sidetube and quartz window contains the metal. The mercury vapour of the pumps is frozen out. If the electric intensity is great enough, and the pressure and temperature good, we get a brilliant blue discharge. It was found that another type of ring discharge could be obtained. (See the preceding paper in these

¹⁾ Compare MOHLER: Excitation of Alkali Spark Spectra. Bureau of Standards. No. 505, p. 131, 1925.

Proceedings). In the centre of the bulb I observed a green yellow axis. ("green" arcspectrum?)

The impurities are hydrogen (H_α and H_β) and sodium (D lines). The ratio of the arc and spark lines of potassium appearing on the plates depends upon the part of the bulb focused on the slit.

The spectra were photographed ¹⁾ with a grating spectrograph (ROWLAND mounting), having a concave grating (8×5 cm, total number of lines; 51949, radius of curvature 1.98 M.), the dispersion being approximately 8.7 \AA per millimetre (first order). We have measured in the 1st and 2nd orders with the standard ironlines as comparison spectrum.

The error of measurement might be approximately $\pm 0.03 \text{ \AA}$.

TABLE 2.

Element	BOHR—STONER scheme for electron distribution													Ionization potential (Volts)	Ratio
	1 ₁	2 ₁	2 ₂ (1+2)	3 ₁	3 ₂ (1+2)	3 ₃ (2+3)	4 ₁	4 ₂ (1+2)	4 ₃ (2+3)	4 ₄ (3+4)	5 ₁	5 ₂ (1+2)	5 ₃ (2+3)	6 ₁	
He I	2	—	—	—	—	—	—	—	—	—	—	—	—	24.5	2.8
Li II	2	(1)	—	—	—	—	—	—	—	—	—	—	—	62.1	
Ne I	2	2	2+4	—	—	—	—	—	—	—	—	—	—	21.5	1.8
Na II	2	2	2+4	(1)	—	—	—	—	—	—	—	—	—	38.9	
A I	2	2	2+4	2	2+4	—	—	—	—	—	—	—	—	15.2	1.6
K II	2	2	2+4	2	2+4	—	(1)	—	—	—	—	—	—	23.7	
Kr I	2	2	2+4	2	2+4	4+6	2	2+4	—	—	—	—	—	12.7	1.7
Rb II	2	2	2+4	2	2+4	4+6	2	2+4	—	—	(1)	—	—	21.0	
Xe I	2	2	2+4	2	2+4	4+6	2	2+4	4+6	—	2	2+4	—	10.9	1.6
Cs II	2	2	2+4	2	2+4	4+6	2	2+4	4+6	—	2	2+4	—	(1) 17.6	

4. Structure of the spectrum.

The arcspectra of the alkali metals consist of a doublet system ²⁾ and are not so very complicate. The spark spectra on the contrary are very rich in lines and have a complex structure. These spectra resemble the arc spectra of the rare gases in accordance with the displacement law. (See Table 2). It is only in the case of *HeI* and *NeI* that series arrangements have been disentangled. In the spark spectra of the alkali metals series have not yet been traced ³⁾. In the spark spectrum of

¹⁾ My thanks are due to Miss LUB for the assistance in the photographic work.

²⁾ P. ZEEMAN has established that *Li* has a doublet system too. Phys. Z. S. 14, 1913, p. 405.

³⁾ For series in *Li II* see: DIK. Dissertatie. Amsterdam. 1922.

H. SCHULER: Naturw. 12. 1924; p. 579. Ann. d. Phys. 76. 1925. p. 293.

M. MORAND: C. R. 178. 1924, p. 1528. 1701. 1897.

S. WERNER: Nature. 115. 1925. 191.

SUGIURA: Journal de Phys. et le Radium. Oct. 1925, p. 323.

Rb.¹⁾ and Cs.²⁾ however, it has been found possible to arrange many of the lines in groups showing constant differences of wave number. In the case of the spark spectrum of K, there should be analogy with the arc spectrum of argon (red spectrum). This spectrum is rich in lines and only constant differences are known^{3) 4) 5)}. NISSEN⁶⁾ has attempted in both cases to arrange the lines in series, but the arrangement is very fragmentary and open to question⁷⁾.

According to the new ideas of the theory, the spectrum of KII will resemble the arc spectrum of Neon too. PASCHEN has given the analysis of this spectrum and disentangled four series of S_i terms, ten of P_i terms and twelve of D_i terms. Recently our knowledge of the spectrum has been extended by the experimental work of HERTZ⁸⁾, MEISSNER⁹⁾, LYMAN and SAUNDERS¹⁰⁾, DORGELO¹¹⁾ and the theoretical considerations of GOUDSMIT¹²⁾ and JORDAN¹³⁾.

Such a structure we expect also in the spark spectra of the alkali metals.

5. Analogy with the arc spectrum of argon.

There is a qualitative analogy between the arc spectrum of argon (red argon)¹⁴⁾ and the spark spectrum of potassium. Both spectra are very rich in lines. It is not possible to study the quantitative relation because the arc spectrum of argon has not yet been analysed. It is however necessary to take new measurements. It is probably like that of neon. Only the constant differences 846.2; 803.1; 606.6 are known¹⁵⁾. Probably we have here the 1 S term differences. HERTZ reported, in analogy with Neon¹⁶⁾ in the extreme ultraviolet¹⁷⁾ a pair of lines. We note that these lines have the difference of $\Delta\nu: \pm 1650$. The lines are probably the $1P-1S_2$ and $1P-1S_4$ combinations.

¹⁾ REINHEIMER: Ann. d. Phys. 71. 162. 1933.

²⁾ SOMMER: Ann. d. Phys. 75. 163. 1924.

³⁾ RYDBERG: Astr. Journ. 6. 338. 1897.

⁴⁾ PAULSON: Phys. Z. S. 15. 831. 1914.

⁵⁾ MEGGERS: Sc. Papers. Bureau of Standards. N. 404. 1918.

⁶⁾ NISSEN: Phys. Z. S. 51. 95. 1915. Astr. Journ. 57. 185. 1923.

⁷⁾ PERCY LOWE a. ROSE: Proc. R. S. Canada. Sect. III. 1924, p. 313.

K. T. COMPTON a. F. L. MOHLER: Critical Potentials. Bulletin of the National Research Council. Vol. 9, part 1. Number 48.

L. BLOCH, E. BLOCH, DEJARDIN: Annales de Physique (10). 1925, p. 465 en 477.

⁸⁾ HERTZ: Physica. 5. 189. 1925. Z. S. f. Phys. 32. 933. 1925.

⁹⁾ MEISSNER: Ann. d. Phys. 76. 124. 1915.

¹⁰⁾ LYMAN a. SAUNDERS: Phys. Rev. 25. 886. 1925.

¹¹⁾ DORGELO: Physica Lorentznummer Dec. 1925. Z. S. f. Phys. 34. 766. 1925.

¹²⁾ GOUDSMIT: Z. S. f. Phys. 32. 111. 1925.

¹³⁾ JORDAN: Z. S. f. Phys. 31. 877. 1925.

¹⁴⁾ The blue Argonspectrum is probably the spark spectrum and contains according to L. BLOCH, E. BLOCH and DEJARDIN (Annales de Phys. (10) 461. 1924) 3 spectra.

¹⁵⁾ See 4 and also: FOWLER: Report on Series in Line spectra. 178.

¹⁶⁾ HERTZ: Z. S. f. Phys. 32. 933. 1925. Physica. 5. 189. 1925.

¹⁷⁾ HERTZ: Communication Nat. Ver. Amsterdam. Dec. 1925.

6. Analogy with the arc spectrum of neon.

Fig. 1 shows the termscheme of this spectrum. There are a number

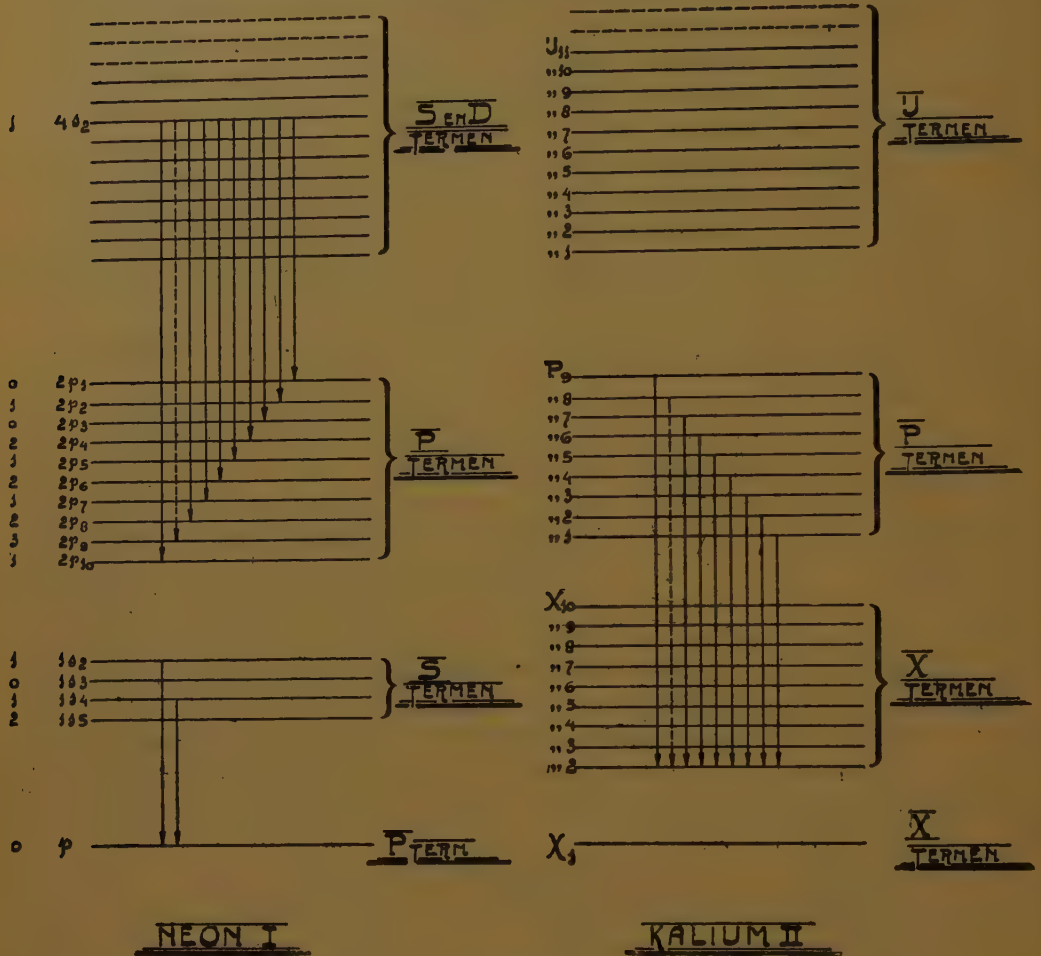


Fig. 1.

of series, (PS) and (PD) combinations, with the nine constant separations of the $2P$ -complex: 1932.3; 121.0; 58.9; 86.4; 456.2; 194.3; 297.4; 167.2; 1399.2, forming groups of ten lines. In different groups members are wanting. (Principle of selection for j).

The three $1S$ -term differences are: 1071.0; 359.4; 417.4. (Fundamental pair $\Delta\nu = 1430$).

In the spark spectrum of potassium I have found, analogous with the spectrum of neon, a termgroup of 9 (10?) levels. We will indicate these terms by P . We get a termscheme, analogous with the Neonscheme. The levels, "beneath" the P complex, are symbolised by X , the levels "above" the P complex by Y . There are groups of 9 lines with the differences: 3180.7; 297.5; 345.5; 623.3; 1039.1; 418.0; 110.4; 362.8. Different groups are wanting a member.

An example of such a group is given in Table 3. (Also indicated in Fig. 1 and on the plate); including some predominant lines of the spectrum.

TABLE 3.

No.	Int.	λ I. Å	ν_{vacuum}	Term-combination
1	9	4829.23	20701.4	P_1-X_2
2	8	4186.24	23881.1	P_2-X_2
3	7	4134.72	24178.6	P_3-X_2
4	6	3995.10	25024.1	P_4-X_2
5	8	3897.92	25647.4	P_5-X_2
6	5	3739.13	26736.6	P_6-X_2
7	6	3681.54	27154.6	P_7-X_2
8	—	—	—	—
9	6	3618.49	27627.8	P_9-X_2

7. Tables.

Table 4 gives the relative values of the terms, termsymbols and term differences. Table 5 gives the lines already classified.

Z.D. refers to the observations by ZEEMAN and DIK.

D. " " " " " DAHMEN.

d.B. " " " " " DE BRUIN.

F.M.M. " " " " " the measurements of critical potentials by FOOTE, MOHLER and MEGGERS.

The main arclines are tabulated too.

The termcombination of some lines has not yet been indicated on the tables. Further in the violet part of the spectrum the *P*-combinations are not so numerous. The following strong lines in the ultraviolet observed by MC. LENNAN form probably a part of a *P* combination. ¹⁾

Int.	λ	ν_{vacuum}	$\Delta\nu$
5	2319.15	43105.9	1089.0
3	2262.0	44194.9	416.5
6	2240.89	44611.4	475.8
3	2217.23	45087.2	

We will report our measures in the violet in another paper.

The *X* termcomplex combines *not* with the *Y* termcomplex. A few combinations however are present. It is not certain whether these lines are perhaps "forbidden lines" or combinations by chance. ²⁾ (Table 6).

¹⁾ From the measures by SCHAUER the relative terms: $Z_1 = -35460$ and $Z_2 = -37002$ are probable.

²⁾ The "forbidden" line $1s-3d$ 4642 Å of the arcspectrum was also with faint intensity present. Compare:

FOOTE, MOHLER and MEGGERS: Astr. Journ. 55, 1922, p. 145—156.

DATTA: Proc. R. S. 101, 1922, p. 539—547.

MOHLER: Bureau of Standards: N. 505, April 1925.

TABLE 4 (Term-Table).

Relative value of the term	Termdifference	Termsymbol	J ¹⁾
0	18501.6	X_1	2
18501.6	730.0	X_2	2
19231.6	199.3	X_3	1
19430.9	1059.8	X_4	0
20490.7	436.2	X_5	1
20926.9	217.2	X_6	2
21144.1	1312.0	X_7	0
22456.1	4373.9	X_8	1
26830.0	691.4	X_9	3
27521.4		X_{10}	2?
39203.0	3180.1	P_1	1
42383.1	297.1	P_2	3
42680.2	845.5	P_3	2
43525.7	623.3	P_4	1
44149.0	1089.3	P_5	2
45238.3	418.0	P_6	1
45656.3	110.3	P_7	2
45766.6	362.8	P_8	0
46129.4		P_9	1
68409.6	160.5	Y_1	—
68570.1	417.4	Y_2	2
68987.5	1734.1	Y_3	1
70721.6	291.8	Y_4	0
71013.4	386.1	Y_5	1
71399.5	450.9	Y_6	1
71850.4	1210.5	Y_7	2
73060.9	660.1	Y_8	—
73721.0	1469.8	Y_9	3
75190.8	3927.9	Y_{10}	2
79118.7		Y_{11}	—

¹⁾ The column with the J -values has been added in the English translation.
 $P_{10} = 50770.7$ ($J=0$) $P_{10}-P_9 = 4641.3$. X_1 and Y_1 are doubtful.

TABLE 5.

	λ		λ I. Å		λ I. Å	ν_{vacuum}	Term-combination	F. M. M.	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.				
				3	7699.0	12985.1	1s—2p ₂	3.5	
				3	7664.9	13042.8	1s—2p ₁	3.5	
				2	6939.5	14406.3	2p ₁ —3s		
				2	6911.8	14464.1	2p ₂ —3s		
1	\pm 6594			2	6595.00	15158.8	P ₃ —X ₁₀		
2	\pm 6562			8	6562.83	15233.0	H α		
1	6427.9	1	6427.690	5	6427.96	15552.7	P ₂ —X ₉		
8	6307.2	2	6307.240	7	6307.29	15850.2	P ₃ —X ₉		
5	6246.5	1	6246.465	6	6246.59	16004.3	P ₄ —X ₁₀		
15	6120.2	2	6120.219	8	6120.27	16334.6			
				1	6012.41	16627.6	P ₅ —X ₁₀		
				2	5969.64	16746.8	P ₁ —X ₈		
				2	5831.99	17142.0	2p ₁ —5d		
				1	5812.30	17200.1	2p ₂ —5d		
		5	5801.75	2	5801.75	17231.4	2p ₁ —4s		
				2	5782.44	17288.9	2p ₂ —4s		
1	\pm 5772			4	5772.32	17319.3	P ₅ —X ₉		
		1	5642.674	5	5642.73	17716.9	P ₆ —X ₁₀		
1	\pm 5536			3	5536.01	18058.5	P ₁ —X ₇		
				2	5512.69	18134.9	P ₇ —X ₁₀		
4	5469	2	5470.065	6	5470.13	18276.2	P ₁ —X ₆		
		3	5359.684	1	5359.70	18652.5	2p ₁ —6d	6	
				1	5339.91	18724.9	2p ₁ —5s	6	
3	5314	1	5310.208	5	5310.24	18826.3	P ₇ —X ₉		
8	5056.0	1	5056.182	7	5056.27	19771.9	P ₁ —X ₄	40	
				1	5017.34	19925.5	P ₂ —X ₈		
15	5005.5	4	5005.586	8	5005.60	19972.0	P ₁ —X ₃	40	
				1	4964.72	20136.1	2p ₁ —8d	6	

TABLE 5 (Continued).

	λ		λ I. Å		λ I. Å	ν_{vacuum}	Term-combination	F. M. M.	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.				
5	4943.2			6	4943.24	20224.0	P_3-X_8	40	
				4	4861.35	20564.7	$H\beta$		
30	4829.2	2	4829.212	9	4829.23	20701.4	P_1-X_2	20	
3	4744			4	4744.92	21069.2	P_4-X_8		
15	4659.8	1	4659.317	7	4659.38	21456.2	P_2-X_6	40	
30	4608.5	5	4608.425	7	4608.45	21693.2	P_5-X_8	25	
10	4596.0	2	4595.613	7	4595.65	21753.6	P_3-X_6		
30	4505.6	4	4505.340	6	4505.33	22189.7	P_3-X_5	20	
20	4467.5	3	4466.658	5	4466.65	22381.8	P_4-X_7	40	
9	4455.5			2	4455.00	22440.4	Y_2-P_9		M. L.
10	4423.6	1	4423.716	3	4423.73	22599.0	P_4-X_6	40	4454 ± 0.5
30	4388.3	3	4388.129	7	4388.16	22782.2	P_6-X_8	16	
		1	4383.780	0	4383.80	22804.8	Y_2-P_8		?
		1	4374.870			22851.4	Y_3-P_9		
10	4365.1	2	4362.865	5	4362.96	22913.8	Y_2-P_7		
				1	4354.29	22959.5	P_2-X_4		
30	4339.9	3	4339.977	5	4340.03	23034.9	P_4-X_5		
				2	4317.85	23153.2	P_2-X_3		?
30	4309.5	4	4309.076	7	4309.10	23200.2	P_7-X_8	16	
		1	4305.265			23220.9	Y_3-P_8		
30	4305.0	3	4304.937	7	4305.00	23222.3	P_5-X_6	16	
9	4288.6	1	4288.651	4	4288.70	23310.5	P_8-X_8		
8	4285.1	1	4284.853	3	4284.89	23331.2	Y_3-P_7		Also: Y_2-P_6
30	4263.5	7	4263.312	7	4263.40	23448.8	P_3-X_3	16	
30	4225.7	5	4225.605	7	4225.67	23658.2	P_5-X_5	16	
30	4223.2	5	4222.975	7	4222.97	23673.3	P_9-X_8	16	
9	4208.9	1	4209.498	4	4209.49	23749.1	Y_3-P_6	20	
30	4186.2	9	4186.226	8	4186.24	23881.1	P_2-X_2	16	

TABLE 5 (Continued).

λ		λ I. Å		λ I. Å	ν_{vacuum}	Term-combination	F. M. M.	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.			
30	4149.1	5	4149.171	7	4149.19	24094.3	P_6-X_7	16
30	4134.7	6	4134.721	7	4134.72	24178.6	P_3-X_2	16
30	4115.1	3	4114.952	6	4114.99	24294.6	P_4-X_3	16
		1	4112.071	4	4112.14	24311.4	P_6-X_6	
15	4093.5	1	4093.697	5	4093.69	24420.9	Y_2-P_5	
10	4065.2	1	4065.209	4	4065.23	24591.9	Y_4-P_9	
		10	4047.272	2	4047.24	24701.2	$1s-3p_2$	6
		10	4044.174	2	4044.17	24720.0	$1s-3p_1$	6
15	4042.5	2	4042.594	6	4042.59	24729.6	P_7-X_6	
10	4039.9	1	4039.692	4	4039.69	24747.4	P_6-X_5	
10	4024.9	1	4024.920	4	4024.88	24838.3	Y_3-P_5	40
9	4018.9	1	4017.509	4	4017.52	24884.0	Y_5-P_9	
10	4012.2	1	4012.014	5	4012.10	24917.6	P_5-X_3	40
15	4001.1	5	4001.200	7	4001.24	24985.2	P_9-X_7	16
10	3995.0	3	3995.321	6	3995.10	25024.1	P_4-X_2	25
8	3992.0	1	3991.775	4	3991.80	25044.3	Y_2-P_4	
15	3972.8	3	3972.551	6	3972.58	25165.4	P_7-X_5	25
15	3966.7	3	3966.687	6	3966.72	25202.6	P_9-X_6	20
		2	3959.777	3	3959.84	25246.4	Y_5-P_8	
		3	3956.099	3	3956.10	25270.3	Y_6-P_9	
15	3955.5	6	3955.207	6	3955.21	25276.0	P_8-X_5	20
10	3943.3	4	3942.505	6	3942.53	25357.2	Y_5-P_7	20
9	3934.6	1	3934.304	5	3934.36	25410.0		
9	3927.3	1	3926.338	5	3926.36	25461.7	Y_3-P_4	
9	3923.8	1	3923.053	5	3923.00	25483.5	Y_4-P_6	20
				3	3900.11	25633.0	Y_6-P_8	
		2	3899.242	3	3899.28	25638.5	P_9-X_5	
15	3898.0	8	3897.870	8	3897.92	25647.4	P_5-X_2	16

TABLE 5 (Continued).

	λ		$\lambda I. \text{\AA}$		$\lambda I. \text{\AA}$	ν_{vacuum}	Term-combination	F. M. M.	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.				
3	3887.2	1	3886.702	2	3886.84	25720.3	Y_7-P_9		
5	3884.5	1	3883.358	3	3883.42	25743.4	Y_6-P_7		
8	3879.2			4	3878.62	25775.0	Y_5-P_6	40	
10	3874.5	1	3873.747	5	3873.74	25807.5	P_6-X_4	25	
10	3861.9	1	3861.412	3	3861.41	25889.9	Y_2-P_3	20	
3	3844.8			1	3844.02	26007.0	P_6-X_3		
				3	3821.30	26161.8	Y_6-P_6		
15	3818.6	3	3817.541	7	3817.50	26187.4	Y_2-P_2	16	
		1	3816.549	6	3816.56	26194.2	Y_7-P_7		
15	3800.8	2	3800.141	6	3800.14	26307.3	Y_3-P_3	20	
15	3783.2	1	3783.192	6	3783.19	26425.2	P_7-X_3	16	
15	3767.1	4	3767.372	6	3767.36	26536.2	P_8-X_3	20	
6	3756.0	1	3756.635	3	3756.62	26612.0	Y_7-P_6		
9	3745.2	3	3744.404	5	3744.42	26698.9	P_9-X_4	25	
9	3739.2	2	3739.125	5	3739.13	26736.6	P_6-X_2	25	
9	3722.1	2	3721.344	5	3721.34	26864.4	Y_5-P_5	25	
9	3716.9	1	3716.594	5	3716.60	26898.7	P_9-X_3	25	
15	3682.3	6	3681.525	6	3681.54	27154.6	P_7-X_2	20	
8	3677.6			3	3676.05	27195.4	Y_4-P_4	25	
10	3670.2	3	3668.627	3	3668.60	27250.4	Y_6-P_5	40	
1	3650.6			2	3647.95	27404.7	Y_8-P_7		
4	3639.8			3	3637.00	27487.4	Y_5-P_4		
9	3627.9	1	3626.390	4	3626.42	27567.6			
15	3618.4	5	3618.429	6	3618.49	27627.8	P_9-X_2	20	
12	3609.4	5	3608.871	5	3608.88	27701.4	Y_7-P_5	20	
2	3593.8			2	3593.22	27822.3	Y_8-P_6		
2	3587.1			2	3586.60	27873.6	Y_6-P_4		
8	3562.5			4	3562.15	28064.7	Y_9-P_7		

TABLE 5 (Continued).

	λ		$\lambda I. \text{\AA}$		$\lambda I. \text{\AA}$	ν_{vacuum}	Term-combination	$F. M. M.$	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.				
20	3530.9	8	3530.707	7	3530.75	28314.6	X_8-P_{10}	16	Mc. L. 3489 ± 0.5
				3	3529.53	28324.3	Y_7-P_4		
				1	3528.51	28332.5	Y_5-P_3		
9	3490.8					(28630.3)	Y_5-P_2		
10	3480.9			6	3481.11	28718.2	Y_6-P_3		
3	3457.4			2	3457.85	28911.5	Y_8-P_5		
				1	3447.40	28999.1	$1s-4p_2$	6	
				1	3446.40	29007.5	$1s-4p_1$	6	
20	3439.9			7	3440.05	29061.1	$Y_{10}-P_9$	20	
2	3427.0			2	3427.13	29170.7	Y_7-P_3		
15	3421.9			4	3421.83	29215.8		20	
1	3417.0			2	3416.76	29259.2			
15	3404.2			6	3404.24	29367.6	Y_2-P_1	20	
9	3392.6			3	3392.63	29467.2	Y_7-P_2		
15	3384.6			6	3384.86	29534.9	$Y_{10}-P_7$	20	
15	3380.3			6	3380.62	29571.9	Y_9-P_5	20	
15	3373.5			6	3373.60	29633.4		20	
2	3356.2			2	3356.51	29784.3	Y_3-P_1		
15	3345.0			6	3345.32	29883.9		20	
2	3338.0			1	3337.67	29952.4	$Y_{10}-P_6$		
3	3258.6			3	3258.81	30677.3	Y_8-P_2		
				5	3290.65	30380.4	Y_8-P_3	20	
3	3253.9			3	3253.98	30722.8			
10	3220.2			4	3220.60	31041.2	$Y_{10}-P_5$	25	
10	3190.0			5	3190.07	31338.2	Y_9-P_2	20	
				2	3189.28	31346.0			
3	3171.8			2	3171.81	31518.6	Y_4-P_1		
6	3157.0			2	3157.15	31665.0	$Y_{10}-P_4$		

TABLE 5 (Continued).

	λ		λ I. Å		λ I. Å	ν_{vacuum}	Term-combination	F. M. M.	Remarks
Int.	Z. D.	Int.	D.	Int.	d. B.				
4	3142.7			2	3142.75	31810.0	Y_5-P_1	20	
15	3104.9			6	3105.00	32196.8	Y_6-P_1		
8	3074.7			3	3075.00	32510.9	$Y_{10}-P_3$		
20	3061.7			5	3062.18	32647.0	Y_7-P_1	20	
3	3047.0			2	3047.16	32808.0	$Y_{10}-P_2$		
9	3030.4			2	3030.43	32989.1	$Y_{11}-P_9$		
1	2950.9			2	2950.88	33878.3	$Y_{11}-P_6$		
5	2809.0			3	2808.99	35589.6	$Y_{11}-P_5$		
5	2777.9			2	2777.89	35987.8	$Y_{10}-P_1$		
9	2743.5			4	2743.55	36438.4	$Y_{11}-P_3$		
10	2550.0			6	2550.02	39203.7	P_1-X_1		
5	2504.6			3	2504.60	39914.6	$Y_{11}-P_1$		
				1	2358.70	42383.2	P_2-X_1		
1	2342.3			3	2342.30	42679.8	P_3-X_1		
				1	2296.79	43525.6	P_4-X_1		?

TABLE 6.

ν_{vacuum} calculated	ν_{vacuum} observed	Int.	λ	Observer	Term-combination
44329.0	44327.6	3	2255.29	Mc. LENNAN	Y_7-X_{10}
44569.5	44569.5	2	2243.0	" "	Y_6-X_9
47482.7	47482.0	1	2105.45	" "	Y_1-X_6
56689.2	56689	0	1764.0 (I. Å)	SHAVER	$Y_{10}-X_2$
57974.6	57971	3	1725.0 (I. Å)	"	$Y_{11}-X_7$

8. Comparison with other observers.

The lines:

1. 6012.41; 2. 5969.64; 2. 5512.69; 1. 5017.34; 2. 4317.85; 3. 3900.11;
3. 3821.30; 3. 3529.53; 1. 3528.51

already calculated from the termscheme were present on the plates. Between the lines 4829 and 4744 are different faint lines, some of these lines are arclines. The lines 3. 6050 and 2. 5730 observed by MC. LENNAN are absent. A group of lines between 4115 and 4057 only recorded by NELTHORPE was absent. NELTHORPE reported that these lines possibly may be enhanced lines of chlorine.

The lines: 1. 3749.1 1. 3727.5 1. 3713.2 tabulated only by EDER and VALENTA are probably lines of *OII*. On some plates there appear a number of new lines with the three above mentioned. We could identify the main lines of the spectrum of *OII*.¹⁾ As to the origin it may be possibly a reduction of the oxide formed filling the tube anew. If the bulb contains O the spectrum of *OII* is present without the arc and bandspectrum. We will investigate this spectrum in connection with the preliminary analysis of CROZE.^{2) 3)}

We record some lines not tabulated by other observers. We could, however, not arrange these lines in the termscheme.

3. 4938.75 2. 3985.66 4. 3932.72 2. 3857.95.

A number of faint lines and some strong lines, only recorded by DAHMEN we could not confirm. It may be possible that the tables of DAHMEN contain lines of the blue spectrum of argon. The strong lines of DAHMEN:⁴⁾

3. 4375.954 4. 4332.024 3. 4041.367 6. 3891.449 and 4. 3787.901 were absent. Perhaps it may be the (blue) argonlines:

3. 4375.95 3. 4332.03 2. 3891.40. The line 3.4041.367 may be perhaps the airline 4041.37. Different faint lines coincide also with argonlines f.i.

1. 4502.946 5. 4502.94.

2. 4420.904 1. 4420.94 (ED. and VAL. 4420.89).

1. 4367.848 1. 4367.78 (" " " 4367.87).

1. 4362.053 2. 4362.05.

1. 4275.204 1. 4275.18.

2. 4072.034 4. 4072.01 (ED. and VAL. 4072.03).

2. 3992.080 2. 3992.05.

9. Critical potentials.

The measurements of the critical potentials of the alkalis by MOHLER are important in connection with the analysis of the sparkspectra. A summary has been given in the following Tables 7 and 8.

1) These lines are also characteristic in some spectra of stars f.i. β Canis majoris.

2) CROZE: Comptes Rendus: 180. 1925, p. 278 and 432.

3) Note added in proof: Recently Prof. A. FOWLER F.R.S. has published a extended investigation about this spectrum.

4) C. f. MOHLER, Bureau of Standards No. 505. 1925, p. 181.

TABLE 7.

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	Observed effects
	54 ± 2	35 ± 2	19 ± 1	16.0 ± 0.5	14 ± 2	Radiation; increase in ionization; spark lines with large currents.
2	—	—	23 ± 1	21.6 ± 0.5	—	Increased radiation; spark lines enhanced with large currents.
3	—	44 ± 2	28 ± 1	25.2 ± 1	21.5 ± 1	Spark lines with low current.

TABLE 8.

Element	V_1	V_2	V_3	V'_1	V'_2
<i>Li</i>	5.4	54	(67.5)	(13.5)	(62.1)
<i>Na</i>	5.1	(31.5)	44	(12.5)	38.9
<i>K</i>	4.3	19.0	28	9	23.7
<i>Rb</i>	4.2	16.0	25.2	9.2	21.0
<i>Cs</i>	3.9	(13.5)	21.5	(8.0)	17.6

V_1 = work required to remove the valence electron from the normal atom (*given by the arc limit*).

V_2 = work required to remove a single electron from the rare gas shell of the normal atom.

V_3 = work of double ionization.

V'_1 = work required to remove the valence electron from the atom ionized from the rare gas shell.

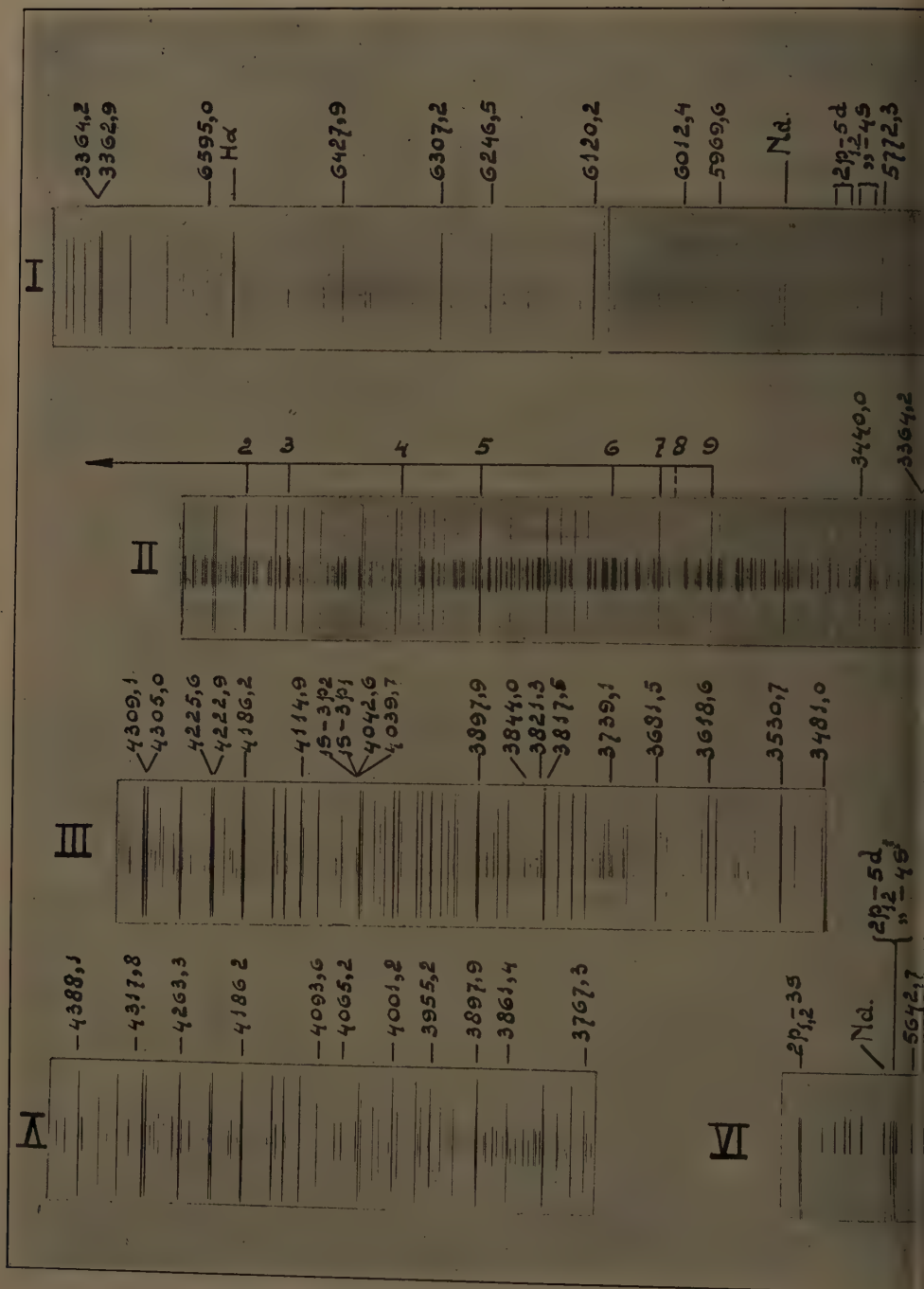
V'_2 = work required to remove one electron from the rare gas shell of the ion with the valence electron removed (*spark spectrum limit*).

$$V_3 = V_2 + V'_1 = V_1 + V'_2.$$

10. Summary.

The spectrum of ionised potassium obtained by means of the electrodeless discharge has been photographed with a grating and measured in the region λ 8000–2000. The accuracy may be $\pm 0.03 \text{ \AA}$. A part of the measures has been recorded in this paper. A number of lines (± 150) has been classified in a termscheme analogous with the scheme of the Neonspectrum.

T. L. DE BRUIN: "THE SPECTRUM OF IONIZED POTASSIUM".



—5005,0
 —4829,2
 —15-3d,2
 —4455,0
 —4309,1
 —4305,0
 —4186,2
 —15'-3p,2

IV

BLAUW-VIOLETTE ONTLADING
 GROEN-GELE " "

K II

—3190,1
 —3129,1
 —3062,1
 —2992,4
 —2938,5
 —2854,3
 —2743,5
 —2550,0
 —2273,9

—2819,3
 —2743,5
 —2689,9
 —2635,1
 —2550,0
 —2440,0
 —2379,3
 —2342,3
 —2273,9

—5536,0
 —5512,7
 —5470,1

—2p-6d
 —5310,2

—5056,2
 —5017,3
 —5005,6

—4943,2

H β

—4829,2

—4744,9

—4659,3

—4608,4
 —4595,6

This research is done in the laboratory of Prof. P. ZEEMAN and I am indebted to Prof. P. ZEEMAN for continued interest and advice.

Description of Plates.

The photographs I, II, III, IV and V give the spectrum of ionised potassium in the region λ 6800 — λ 2270. These were taken with a grating (ROWLAND's mounting). Grating: 8×5 cm total number of lines 51949, radius of curvature 1.98 M., dispersion first order $\pm 8.7 \text{ \AA}$ p.m. M. The main wavelengths are added. The group of 9 lines starting from λ 4829.2 is an example of a (PX)-combination. These group is also indicated in the termscheme (See fig. 1).

The intensity of the first order of this grating was very great. The blue discharge was very brilliant. This is shown by the time of exposition of plate II, which amounted 5 minutes.

Photograph IV gives the ultraviolet part of the spectrum. The plate has been sensitized with paraffine-oil. Photograph VI is taken with a one prism spectograph and gives the two types of discharges which could be obtained.

Note to the English translation.

In a further investigation we could establish the inner quantumnumbers of the terms¹⁾. The *P* terms have quite the same inner quantum numbers as in the case of neon. It is now proved that the terms symbolised by *P* are really *P* terms. Probably it is not the lowest *P* term complex. The term differences of the *P* terms in the spectrum of ionised potassium follow a similar law to those in the case of Neon. In the spectrum of ionised potassium the differences are ± 2 to 3 times larger.

I have found the term $P_{10} = 50770.7$ (with $J=0$) too. The difference $P_{10} - P_9 = 4641.3$. The following lines are yet classified:

2.	5488.06	18216.4	$Y_3 - P_{10}$.
3.	4938.74	20242.2	$Y_5 - P_{10}$ (see 8).
7.	3530.75	28314.6	$X_8 - P_{10}$.
3.	3301.60	30279.6	$X_5 - P_{10}$.

¹⁾ I am indebted to Mr. S. GOUDSMIT some interesting remarks regarding the inner quantumnumbers.

Palaeontology. — "*On the Principal Characters of the Femur of Pithecanthropus Erectus.*" By Prof. EUG. DUBOIS.

(Communicated at the meeting of March 27, 1926).

The left femur was dug up at Trinil in August 1892, during low-water level of the Bengawan, when the most fossiliferous layer of the andesite tuff was again accessible. Ten months earlier the calvarium had been found in that deposit of an ancient river, at 15 m distance *in the same stratigraphic plane*. This circumstance, added to the anatomical relations between the two objects, renders it almost infinitely probable that they represent parts of the same individual.

The **state of petrification** is also the same. The femur has the same deep brown colour as the calvarium. It weighs 1018 gr., which is more than twice the weight of a human femur of the same size, to which the fossil, on the whole, bears a striking resemblance. The volume is 485 cm³. Without the exostosis and without the comparatively small defects this would have been 467 cm³. On an average Negroes and also Australians have a slightly less voluminous femur, at the same length; in Europeans, on the other hand, it is averagely much more voluminous. Assuming the cavities to occupy about half of the total volume of the bone, as in human femora, and the compact bone substance to have a specific weight of about 2.7, as all other fossil bones of the Kendeng-fauna, I estimate that more than 100 cm³, about $\frac{2}{5}$ of all the cavities, are filled up with calcite and some pyrite. The existence of this filling can be observed through the hole in the popliteal surface and by röntgenograms.

The femur is nearly complete and little injured. Some small **defects** can only be judged properly by the study of the fossil bone itself. That hole in the popliteal surface has been caused during the excavation, a piece of compacta of a length of almost 4 cm and of a breadth of from 1 to $1\frac{1}{2}$ cm broke off and got lost. In the same way a piece in the fossa intercondyloidea, about 2 cm long, has got lost, and also a small fragment at the anterior extremity of the condylus medialis. Immediately above its lower edge the condylus lateralis further shows a round impression of the point of a crocodile tooth. Some marks of crocodile teeth are to be seen at the upper portion of the femur. Thus on the front side: in the collum, beside the caput, a shallow impression accompanied with small fractures, and between the linea intertrochanterica anterior and the lower part of the trochanter major, a deeper, round impression, directed obliquely from the inner side and above towards the outer side and below. At the back side: in the middle of the collum a semi-circular impression obliquely

across fragments going from above and the inner side towards below outward; another in the upper corner of the trochanter major, which corner is further broken off; on the outer side of the crista intertrochanterica a large shallow impression at the place of the tuberculum musculi quadrati, and a small, very shallow impression 1 cm lower; a double shallow impression on the trochanter major, in the middle of the surface for the tendon of the musculus gluteus medius. The caput femoris, preserved for the most part, presents however extensive defects on the margin of the globular articular surface, which were probably also caused by crocodiles, so that of that margin only a small part has remained preserved on the upper side, and a still smaller part on the lower side.

The large **exostosis** below the trochanter minor takes the place of the intermuscular connective tissue between the vastus medialis and the adductores, accompanying the arteria and the vena profunda femoris and their rami perforantes. The course of these blood-vessels can clearly be recognized by the grooves and perforations of the exostosis. At the same place as in Man, the musculus adductor brevis has evidently lain behind the exostosis; its lower edge being apparently indicated by that of the exostosis and its hook. On the much smaller excrescence of the inner lip of the linea aspera below the main mass of the exostosis the insertion of the adductor longus is clearly impressed, somewhat more to the front than that of the adductor brevis, which covered it above. The insertion of the adductor longus was about 10 cm long.

Measures. The whole length of the femur in the natural position (measure 2 of RUD. MARTIN's *Lehrbuch der Anthropologie*) is 455 mm.

According to human proportions a body height of 160 to 170 cm has been calculated from this. From particulars of the femur and the calvarium it may however be deduced with certainty that the proportions must have deviated considerably from those of Man, in the direction of those of the Anthropoids, so that the trunk must have been out of proportion longer than in Man.

The length of the diaphysis (measure 5 of RUD. MARTIN) is 373 mm. The sagittal and the transverse diameter of the diaphysis, just below the excrescence of the linea aspera, about in the middle of the length (measure 6 and 7 of RUD. MARTIN) are 29 and 28 mm. The circumference there (measure 8), at the same time the smallest of the diaphysis, is 89 mm.

At the femora of 26 negroes in the Muséum d'histoire naturelle and the Musée Broca of the École d'Anthropologie at Paris I found with lengths from 425 to 494, mean 455 mm., for this circumference on an average 83.7 mm, at the femora of 2 Australians with lengths of 443 and 458 mm a mean circumference of 83 mm; at the femora of 10 Frenchmen with lengths from 414 to 492 mm, mean 444 mm, a circumference of 86 mm, and at the femora of 3 Japanese with lengths from

410 to 422 a mean circumference of 85 mm. The femur of Trinil may, accordingly, be called anything but slender. An impression of slenderness is only due to the absence of the ordinary human "trumpet form" of the lower end. Of the Hylobatides only a short-legged race of *Symphalangus syndactylus* (of Gunung Sago) has a femur which is equally little slender. As with equal length the power of resistance against breaking of a bone increases as the third power of the diameter (or of the circumference) of the diaphysis, *Pithecanthropus* had a femur which was a fifth stronger than on an average that of the negroes. The muscular force was probably also greater in the same proportion; then with the same proportion of trunk and legs, the body weight was almost a third greater.

The equatorial diameter of the caput femoris in the transversal plane is 44.7 mm and the sagittal diameter, perpendicular to it, about 44 mm (measures 18 and 19 of MARTIN).

The distal foramen nutritium lies 196 mm above the lower end of the femur.

The greatest length of the condylus lateralis is 62 mm, that of the condylus medialis 64 mm (measures 23 and 24). In Man the lateral condylus is not always longest; in some cases the medial condylus.

The curvature of the diaphysis (measured according to RIED's method ¹⁾) is 8 mm. The summit of the curve lies at 17½ cm above the patellar part of the articular surface of the knee-joint. In comparison with most human femora this curvature is slight and the summit situated also at a comparatively low point. In an only moderately curved negro femur (New Museums Cambridge, N^o. 12, length 485 mm) I measure 13 mm at 23 cm above the knee-joint. Calculated to the same femur length this would become 12 mm. The femur of *Pithecanthropus* is certainly not straight, as most femora of the Hylobatides are. In a *Hylobates agilis* I find, however, the same curvature of the diaphysis (calculated to the same length) as in *Pithecanthropus*. Particular distinctive significance can, it seems to me, not be assigned to this height of the femur curve. On the other hand I consider it of particular significance that the femur of Trinil exhibits the strongest curvature to the front very low, at about 7 cm above the level of the patellar articular surface, i.e. at the same place where the diaphysis possesses its greatest antero-posterior thickness, because at the backside at this place the buttress of the median wall attains its greatest strength.

The "angle of torsion" (measure 28) is 19°. As in Man this angle is very variable in the Anthropoids, hence without distinctive significance.

The collo-diaphysis angle (measure 29) is 123°.

The angle between the anatomical axis and the perpendicular to the inferior tangent of the condyles (transversal inclination) is 11°, the angle

¹⁾ A. H. RIED, Die Schaftkrümmung des menschlichen Femur. Anthropologischer Anzeiger. Jahrgang I, p. 102—108. München 1924.

of the mechanic axis with this perpendicular 6° . With joined knees (with the soft parts) the breadth over the two great trochanters would consequently not have been more than 32 cm.

The resemblance of the fossil femur to that of Man, in contrast to



Fig. 1.



Fig. 2.



Fig. 3.

the Apes, is very marked in the knee-joint, which was adapted for perfect extension of the leg. This appears in particular when the sagittal line of curvature of the condyles is compared with that of men and apes. From cross-sections of accurate plaster casts of the tibio-femoral part of the cartilage-less medial condylus, according to the line of contact of the condyli with a horizontal plane upon which they roll, I find that in *Pithecanthropus* (fig. 1, natural size) the radii of the spiral line decrease from the front backwards slightly more, i. e. in the ratio of 100 : 37.5, than as a rule in Man, where the proportion of the frontmost and the backmost radius generally deviates little from that in the negro (Anatomical museum Amsterdam, length of femur 471 mm) of fig. 2, i. e. 100 : 46. In the Anthropoids the radii of curvature decrease much less from the front backward, perhaps most in Gorilla. In fig. 3, natural size, of a ♀ Gorilla the ratio is 100 : 64. In these three figures the points above the curve indicate the evolute of the shifting axis of rotation. *Pithecanthropus* seems to outstrip the human mean in this respect; thus also in the transverse curves of the backmost parts of the condyles, as seen from behind perpendicularly to the shaft of the femur. Especially the medial condylus is still flatter there than as a rule in Man. Compare fig. 4, natural size, of *Pithecanthropus* and

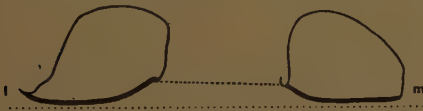


Fig. 4.

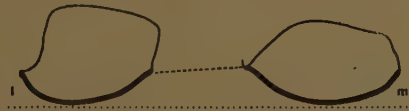


Fig. 5.

fig. 5 of the negro mentioned before (Amsterdam). In that composite articulation, the trocho-ginglymus of the knee-joint, the ginglymus component was even more predominating than in Man, in contrast to the Anthropoids. Rotation of the tibia in the knee-joint thus was of still less importance than in Man, the contrast to the Apes greater.

In the röntgenogram, both in that of the upper end of the femur and the lower end, the "trajectoria" of the human type may be recognized, though on account of the filled cavities they are not so clear as in other thigh-bones.

Two characters distinguish the Trinil femur very decidedly from that of Man. These are in physiological relation to each other, though the first refers to the form of the lower part of the diaphysis and the other to that of the trochanter major at the superior extremity of the femur.

Down to low on the popliteal surface and beginning at more than 11 cm above the level of the patellar articular surface the back side shows a *median swelling* and rounding. Below the linea aspera, which is not strengthened in this femur to a buttress, crista femoris or "pilastre", a median buttress has evidently developed, descending to less than 2 cm above the knee-joint. In Man, on the contrary, the ridge proceeds as a rule, with the external supracondylar line or labium laterale (*l*) of the linea aspera, to the lateral condylus, and accordingly the *lateral* condylus of Man is considered as receiving the most of the pressure of the body-weight. In Pithecanthropus the line of pressure seems to fall between the condyles, accordingly a median buttress placed lower seems to be necessary.

This peculiarity of the Pithecanthropus-femur may be best judged by cross-sections of accurate plaster-casts, which are reproduced here. In



Fig. 6.



Fig. 7.

the figures from 6 to 22, all natural size, the points *a* (before) and *p* (behind) lie in the median plane of the shaft, *m* represents the continuation of the labium mediale and *l* of the labium laterale of the linea aspera. In fig. 6 of the cross-section at only 2 cm above the level of the patellar articular plane the median rounding still exists. This is absent at the corresponding level in the negro mentioned (Cambridge), (fig. 7), though the femur at that place is still somewhat less broad than that of Pithecanthropus. It is also absent in the ordinary European type, as at the femur with exostosis of Strassburg mentioned by SCHWALBE ¹⁾

¹⁾ G. SCHWALBE †, Studien über das Femur von Pithecanthropus erectus Dubois. (Studien über „Pithecanthropus erectus Dubois“. II Teil). Herausgegeben von EUGEN FISCHER. Zeitschrift für Morphologie und Anthropologie. Bd. 21, p. 359. Stuttgart 1921. The cross-sections of this right femur represented here have been reversed for a comparison with the other left femora.

(fig. 8, length of femur 458 mm) and in another type, with large tuberculum supracondyloideum, of a Dutchman (fig. 9, length of femur 454 mm). Fig. 10 is the cross-section of the Trinil femur at 3,2 cm above the articular surface, and fig. 11 at 4 cm above this surface. Fig. 12 represents, at corresponding level, the cross-section of the femur of the negro (Cambridge), fig. 13 at a height of 4 cm that of the Strassburg-femur,



Fig. 8.

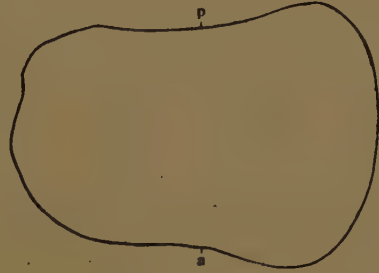


Fig. 9.

fig. 14 of one of the five roundest femora at the corresponding level (femur *H*) found by MANOUVRIER¹⁾ among a thousand. He explains this form by the weakening of the lateral prolongation of the linea aspera or "prolongement pilastrique" in consequence of smaller extension of the origin of the musculus vastus intermedius ("muscle crural") down-

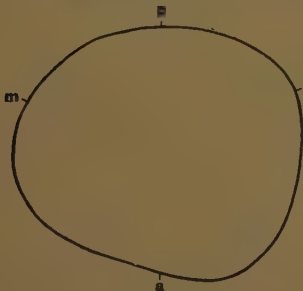


Fig. 10.

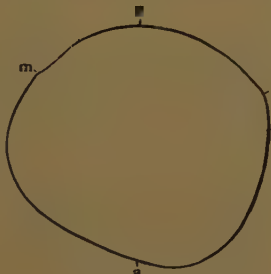


Fig. 11.

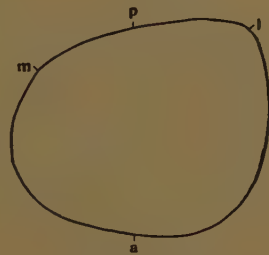


Fig. 12.

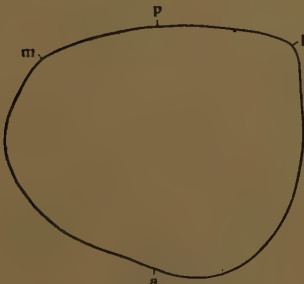


Fig. 13.

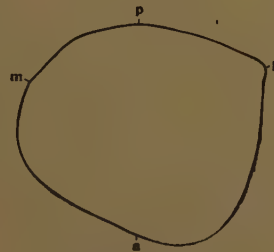


Fig. 14.

¹⁾ L. MANOUVRIER, Deuxième étude sur le *Pithecanthropus erectus*. Bulletin de la Société d'Anthropologie de Paris. Tome 6 (4e série), p. 560 e. v. 1895.

ward and outward. Among many human femora of various races also HEPBURN¹⁾ found some with strong median convexity at corresponding level, but in no human femur described or known to me does this convexity rise in the same degree above the joining line of *m* with *l*, and does it bulge upwards to such a buttress-like median swelling as in *Pithecanthropus*. At 7.2 cm above the articular surface the median convexity of the back side of the femur of *Pithecanthropus* is most pronounced (fig. 15). In the negro of Cambridge (fig. 16) the space between *m* and *l* is only slightly arched at the same level, and in the Strassburg-femur with exostosis (fig. 17) for the greater part flat. At 11 cm above the articular plane the fossil femur shows already this median buttress of the back side (fig. 18) beside the external lip of the *linea aspera*, the internal lip is absent. Fig. 19 is the cross-section of the Trinil femur at 17 cm above the knee joint, and fig. 20 of the Strassburg-femur at 16 cm. Fig. 21 is the cross-section of the Trinil femur at 20 cm, through the excrescence in front of the adductor longus muscle, where on the outside of the *linea aspera* the greatest excavation through the vastus lateralis exists, and fig. 22 at 22½ cm, just under the large exostosis.



Fig. 15.



Fig. 16.



Fig. 17.



Fig. 18.



Fig. 19.

¹⁾ D. HEPBURN, The Trinil Femur (*Pithecanthropus erectus*) contrasted with the Femora of various Savage and Civilised Races. *Journal of Anatomy and Physiology*, Vol. 31, p. 1. 1897.

In these cross-sections of the fossil femur the complete absence of an *angulus medialis* also strikes the eye, in contrast with the human femur,



Fig. 20.



Fig. 21.



Fig. 22.

but in accordance with this bone in Apes. In Man the inner side (as *angulus medialis*) remains free from attachment of muscles; in the Apes, on the other hand, the origin of the vastus intermedius or of the vastus medialis continues on the inner side of the femur, enveloping this bone continuously. Thus it seems also to have been in *Pithecanthropus*.

It seems to me that the very peculiar shape of the lowest third part of the diaphysis of the femur of *Pithecanthropus* should be attributed to static and mechanic causes, as was already indicated above. But to other static and mechanic properties of a bone must also correspond other muscular arrangements. Modifications of the form of the human femur, which undoubtedly indicate modified static and mechanic qualities, are always accompanied by corresponding modified muscular actions, hence modified muscle attachments. It has further appeared from many measurements that muscular force is the greatest of the forces acting on the bones. Comparison of large and small homomorphous (related) species of animals, as Rat and Mouse, Lion and Cat, shows moreover that the relative strength of the bones is not determined by gravity (the body-weight), but by muscular force.

Now it is clearly to be seen on the femur of *Pithecanthropus* that the insertion of the adductor magnus below the linea aspera was different from that in *Homo*. Of the labium mediale, running in Man to the epicondylus medialis, only two small knobs are to be seen, at $11\frac{1}{2}$ and 10 cm, and a line between 5 and 3 cm above the level of the patellar articular surface. The small development of this part of the labium mediale is particularly striking by the side of the other, very strongly modelled muscle insertions. This, together with the rotundity of the diaphysis on the inner side, and the existence of the buttress-shaped median swelling, are circumstances which render a fleshy median attachment of the portio pubica (portio nervi obturatorii) of the *adductor magnus* in *Pithecanthropus* probable, a development and way of insertion differing from that of Man, but occurring, with few exceptions, in the Monkey tribe, through which the function of this muscle is modified.

Many years ago I was enabled by Professor BOLK to examine this insertion on muscle preparations of a number of Apes. I may now be allowed to represent the principal results of this investigation in the figures 23 to 30, in which *Am* indicates the attachment of the portio nervi obturatorii of the adductor magnus, *I* of the portio nervi ischiadici (musculus ischio-femoralis), *B* of the caput breve of the biceps femoris. In *Anthropopithecus troglodytes* (fig. 23), *Simia satyrus* (fig. 24), *Nasalis larvatus* (fig. 25), *Cynomolgus fascicularis* (fig. 26), *Cynopithecus niger* (fig. 27), also *Macacus nemestrinus* and *Cynocephalus maimon*, further *Ateles paniscus*

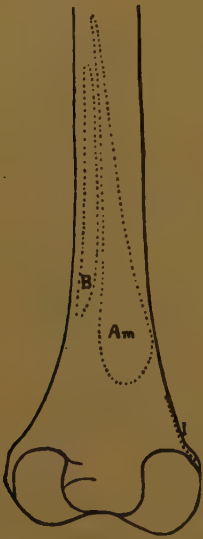


Fig. 23.

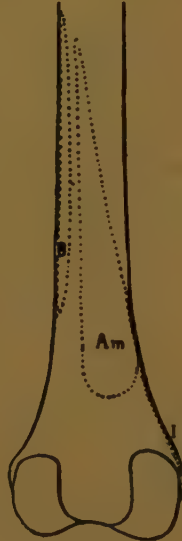


Fig. 24.



Fig. 25.



Fig. 26.



Fig. 27.



Fig. 28.



Fig. 29.



Fig. 30.

(fig. 28), *Am* fleshy and broad, is extended low as far as into the planum popliteum, which in many Apes, among others in the Chimpanzee and the Orang-utan, exhibits a median convexity certainly caused in the first place mechanically. In the movements of all these species in the trees this insertion of the very powerful muscle is particularly serviceable to bring the centre of gravity of the body from outside above the fixed leg, and at the same to turn the front to the other side. Only in the Hylobatides: *Hylobates javanicus* (fig. 29), *H. agilis* and *Symphalangus* the insertion of this part of the adductor magnus, though also a powerful muscle, terminates partly tendinous at great distance above the popliteal surface. To the wonderfully elastic skipping movements of the Hylobatides belongs a long femur with more tendinous insertion lying closer to the coxal joint.

On the femur of *Pithecanthropus* there are no traces to be found of an insertion similar to that of Man (fig. 30); that at the labium mediale of the linea aspera is seen to end abruptly where the median buttress and swelling begins, which gradually broadens over the back side of the femur to low in the planum popliteum, in the same way as this adductor muscle does in most Apes, Monkeys and Baboons. This induces me to assume that in *Pithecanthropus* the muscle, broadening downward, was attached fleshy at the middle of the posterior surface of the femur to low in the planum popliteum. Longitudinal slight grooves there are undoubtedly traces of this insertion. In virtue of this insertion — or rather this origin — the muscle possessed, in deviation from its function in Man, an action going hand in hand with the adducing action, of rotating the femur strongly outwards, or rather an action bringing, with fixed leg, the centre of gravity of the upper part of the body from outside above this leg, and turning at the same time the front to the other side, as in most Apes. For the rest all the muscles that rotate the femur outwards seem to have possessed this power in a high degree. The inward rotation by the portio ischiadica was, on the contrary, probably comparatively weak.

Another special character that very definitely distinguishes the femur of *Pithecanthropus* from that of Man, and which is in physiological relation to the just described character, is the position of the *trochanter major in the continuation of the diaphysis*. Fig. 31 (like fig. 32 postero-lateral view from photograph at a great distance) accurately indicates this position at $\frac{3}{4}$ natural size. The trochanter major shows the same prominent diagonal line *e*, which on its quadrilateral external surface extends from the posterior-superior to the anterior-inferior angle, as in Man, with the same triangular surface above it, where this line alone (in the case that there is a bursa mucosa on the triangular surface) or together with the triangular surface (in the case of non-existence of a bursa) serves for the attachment of the tendon of the *glutaeus medius*. Below the line *e*, at the place where in Man mostly a bursa is situated

under that part of the tendon of the *glutaeus maximus* which is attached to the fascia lata, the external surface of the trochanter major shows, as



Fig. 31.



Fig. 32.

individual peculiarity, an excrescence, which evidently originated from connective tissue, in the same way as the large exostosis below the trochanter minor. As in many cases in Man, and similarly in the Apes, the tendon of the *glutaeus medius* in *Pithecanthropus* seems to have been attached not only at the prominent diagonal line, but also at the trigonal part of the surface of the great trochanter up to the superior border. Behind the said excrescence and along the *crista intertrochanterica* the bone is smooth. The posterior border with the whole great trochanter is directed *vertically upward*. In Man, on the other hand, as well as in almost all Apes, Monkeys and Baboons the posterior border with the whole great trochanter has an oblique direction upwards and *forward* (fig. 32, femur of a Dutchman). In *Pithecanthropus* the great trochanter is not placed on the diaphysis slanting forward as in Man and in the whole Monkey tribe, with the exception of two genera, but forms as it were, a prolongation of the diaphysis upwards.¹⁾ This points to a peculiar condition of the *musculus glutaeus medius* (and the *m. gl. minimus*) in *Pithecanthropus*. The direction of the trochanter major of Man, slanting forward, is undoubtedly a consequence of the forward expansion of the ilium and hence of the origin of the *glutaeus medius* and of the *glutaeus minimus*, in front of the great trochanter.

¹⁾ This is what in 1894 I expressed as concave form of the *crista intertrochanterica*, without then observing a difference in the form of the great trochanter.

Although in Man the thigh, which is bent in the Apes, is brought in a line with the body, and consequently the trochanter is turned forward, the ilium has expanded equally much in the same direction, not being overtaken by the turned trochanter. In the Apes, *sensu generali*, the ilium has expanded forward much less far, if at all, but nevertheless the trochanter major generally points upwards and *forwards*, on account of the habitually bent position of the femur. Thus also in *Symphalangus*, which though he can stretch the femur fairly far, possesses a comparatively heavy, long, and broad trunk and heavy arms, like Gorilla, through which the ossa ilii are developed somewhat more "basin"-shaped than in *Hylobates*, the crests of the ilia diverge, and the two spinae anteriores superiores are situated relatively far to the front. In consequence of this the direction of the powerful *musculus gluteus medius*, which inserts at the upper border of the great trochanter, is such, that also with extended femur, the trochanter major points upwards and forward. This is different in the so closely allied genus *Hylobates*. Possessing on an average absolutely equally long femora as *Symphalangus*, which certainly are not less extensible, the species of this genus have an absolutely and relatively shorter and narrower trunk. Consequently the ossa ilii are not broadened and not expanded forward, but they are narrow, and placed with their crests almost or entirely transverse. The tendon of the *gluteus medius*, which muscle is equally powerful in relation to the size of the body, is in consequence of this, also directed more vertical towards the great trochanter, and not obliquely backwards as in *Symphalangus*, and that process is not placed on the diaphysis obliquely upwards and forwards, but in its prolongation, as in *Pithecanthropus*.

A similar but less sharp difference in the shape of the great trochanter as between *Hylobates* and *Symphalangus* exists between Chimpanzee and Gorilla, owing to the relatively heavier trunk, and consequent forward expansion of the ilium of the latter.

Accordingly *Pithecanthropus* cannot have possessed a human-shaped pelvis, but as the femur could to all appearance be extended to a human degree, the pelvis may have been comparatively more human than that of *Hylobates* and Chimpanzee. The tendon of the *gluteus medius* was inserted more posteriorly of the centre of rotation of the hip-joint, and produced, therefore, a stronger outward rotation constantly accompanying the abduction. With fixed leg the strong muscle brought the centre of gravity of the body from the other side above that leg, and turned the front of the trunk to the other side.

With such an unhuman pelvis the locomotion of *Pithecanthropus* cannot have been exclusively, perhaps not even chiefly, on the ground. The erect type was not perfectly developed. For not the whole structure of the body is in keeping with the erect posture and gait. This might already be inferred — judging from the preserved part of the skull — from the undoubtedly backward position of external auditory meatus, and with it of

the condyli occipitales and the foramen magnum, and from the not human slope of the nuchal plane of the occipital bone, in which characters *Pithecanthropus* occupies a place about halfway between Man and the Anthropoids.

The movements in the hip-joint described and the greatly predominating hinge-movement component in the knee-joint render it probable that *Pithecanthropus* was less ground-walker than tree-climber, but did not climb with a prehensile foot, in the way of the Apes.

In the ordinary locomotion of *Homo sapiens* and *Homo neandertalensis* each leg supports alternately the body in such a way that with transversal knee axis placed as much as possible horizontally, the condylus lateralis is chiefly loaded. For this reason the diaphysis is thicker above this condylus than above the condylus medialis — and also as a rule than between the two condyli — and the linea aspera, which may be strengthened to crista femoris or "pilastre", continues from the middle, below the bifurcation of the labia of the linea aspera, in the lateral thickening of the diaphysis mentioned.

In *Pithecanthropus*, on the other hand, the diaphysis was thickened *in the middle* also below this point of bifurcation, up to close above the knee-joint; mostly opposite the point of the strongest forward curvature. Evidently the line of pressure lay here on the inner side of the condylus lateralis, because in the usual locomotion the supporting leg was not placed near the line of gravity of the body (though the diaphysis makes a human angle with the transverse axis of the knee-joint), but further outward; consequently the transverse axis did not remain horizontal, but descended obliquely inwards, and the pressure weighed on *the inner border of the foot*. The leg then remained in abducted position, and at the same time turned outwards on account of the peculiar attachment of the musculus gluteus medius, which muscle certainly as a whole produced a strong outward rotation of the femur combined with the abduction. The leg on extension being still less adapted for rotation in the knee-joint than that of Man, was on adduction, through the peculiar attachment of the musculus adductor magnus also turned outside with the foot, a necessary condition if the most usual locomotion consisted in climbing trees with alternately extended legs. Hence the two muscles mentioned, when bringing the trunk above the extended and fixed leg, turned the former at the same time with its front to the other side. The femur of *Pithecanthropus* was, therefore, also fit for locomotion on the ground, but by no means adapted so exclusively for it as in *Homo sapiens* and *Homo neandertalensis*. Yet the erect walking on the long legs, which were adapted for perfect extension, may have been distinguished by great speed, if very long arms served at the same time as a kind of crutches. If *Pithecanthropus* had long arms, these could enable him to perfection to climb thick solitary trees projecting high above their surroundings, in the same way as the

aborigines of Australia according to LUMHOLTZ's description (as figured at foot), but without the aid of a rope. To this specialization, which includes an erect gait on the ground, his high cephalisation, compared to that of the anthropoid Apes, is, in my opinion, to be ascribed.



Physics. — "*The Distribution of Thermal Energy in Organic Molecules*".

By DONALD H. ANDREWS.¹⁾ (Supplement N^o. 57*b* to the communication from the Physical Laboratory at Leiden). (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of May 29, 1926).

§ 1. Because of the rapidly accumulating data in the fields of specific heat and infra red spectra which promise to provide a new method of studying organic compounds, there is arising a need for some theory to correlate these observations as a guide for future work. To fill this need the following theory, or perhaps better, working hypothesis is presented which offers an explanation of the shape of the typical specific heat curve, leading, it is hoped, to a better understanding of the band spectra.

The fundamental postulate of this theory is that the organic molecules in a crystal can be treated as a dynamical system having a number of independent modes of vibrations into which the molecular thermal motions can be resolved. Each one of these modes of vibration is assumed to act as a simple Planck oscillator, so that the average amount of its energy and heat capacity depends only on its temperature and characteristic frequency. Thus for a single degree of freedom in a gram molecule the heat capacity is

$$C_v = \left[\frac{\left(\frac{\theta}{T} \right)^2 e^{\frac{\theta}{T}}}{(1 - e^{\theta/T})^2} \right] = R F_E \left(\frac{\theta}{T} \right).$$

T is the absolute temperature. θ , the „converted frequency”, is the true characteristic frequency of the vibrator multiplied by $\beta = 4.778 \times 10^{-11}$, the ratio of PLANCK's constant, h , and BOLTZMANN's constant, k . The symbol F_E is used to denote the EINSTEIN²⁾ specific heat function which is multiplied by R instead of $3 R$ because here it is applied to only a single degree of freedom, instead of to 3, the case of the monatomic solid for which it was developed.

To illustrate the analysis of the motions of the molecule and atoms into these independent modes of vibration, the benzene molecule is selected as an example, and the vibrations are discussed in three parts, namely vibrations of the molecule as a whole, of the CH groups, and of the H atoms.

¹⁾ National Research Fellow (U. S. A.) on a fellowship of the International Education Board.

²⁾ A. EINSTEIN, *Annalen der Physik* (4) 22, 180, 1907.

§ 2. We may expect the vibrations of the *molecule as a whole* to resemble the vibrations of the atoms in a monatomic solid where, according to DEBIJE's theory¹⁾ there are not only the translational vibrations of the individual atoms to be taken into account but also the elastic motions of the crystal lattice. In the case of benzene, in addition to these degrees of freedom accounted for directly by DEBIJE's theory, we must also expect three degrees of freedom for rotational motion because a molecule like benzene certainly has a very appreciable moment of inertia, although individual atoms²⁾ apparently do not. The complete treatment of this problem, while extremely interesting, involves great difficulties in theory and has not been attempted, but in a simple way it is possible to get approximate values for the frequencies involved.

The molecule is treated as a hexagonal frame with the mass, the positive nuclei of carbon, at the corners. We assume that the forces which resist the motion of this frame act on the carbon atoms, and that these forces are the same for each atom and resist the motion of the atom in any direction to roughly the same amount. According to the theory of the harmonic oscillator, the frequency of translational motion, ν_T , along any axis can be expressed as

$$\nu_T = \frac{1}{2\pi} \sqrt{\frac{K_1 + K_2 + \dots K_6}{6m}}$$

where $K_1 \dots K_6$ are the restoring forces per unit displacement of the molecule along the axis chosen, acting on carbon atoms 1 ... 6; m is the mass of the carbon atom. Considering the frequency of rotation, ν_R , about any axis:

$$\nu_R = \frac{1}{2\pi} \sqrt{\frac{K'_1 r_1^2 + K'_2 r_2^2 + \dots K'_6 r_6^2}{m(r_1^2 + r_2^2 + \dots r_6^2)}}$$

where $r_1 \dots r_6$ are the distances from carbon atoms 1 ... 6 to the axis of rotation, and $K'_1 \dots K'_6$ are similarly the forces per unit linear displacement. Since we have postulated that all the K 's and K' 's have about the same value for any case, it is seen that all the values of ν_R and ν_T should be roughly the same. From those considerations we write for the motions of the molecule as a whole:

$$(C_v)_{\text{molecule}} = 6 R F_D \left(\frac{\theta_m}{T} \right)$$

where F_D is the DEBIJE specific heat function which is here multiplied by $6 R$ instead of $3 R$ as in DEBIJE's original formula because we have

¹⁾ P. DEBIJE, Ann. Physik. (IV), 39, 789 (1912).

²⁾ For treatment of inorganic compounds see NERNST, Vorträge über die kinetische Theorie der Materie und der Elektrizität, Göttingen, 1914. Also W. M. LATIMER, Jour. Am. Chem. Soc. 44, 90, 1922.

here the six degrees of freedom instead of three as in the case of the monatomic solid. θ_m is the "average", so to speak of the converted frequencies of each of the six degrees of freedom.

The next step is to secure a numerical value of θ_m so that the heat capacity may be calculated. For this purpose the only possibility seems to be the formula of LINDEMANN ¹⁾ which relates the frequency, θ_m , to the melting point, T_m , molecular weight, M , and atomic volume V , as follows

$$\theta_m = 3.08 \times 10^{12} \times \beta \sqrt{\frac{T_m}{MV^{2/3}}}$$

In employing for a large complex molecule this formula which was developed for a monatomic solid it does not seem reasonable to use the *molecular* volume for V , which as cube root represents the distance the molecule must vibrate through to rupture the intermolecular bonds. In a crystal of benzene with the molecules stacked together like plates, as *X*-ray analysis indicates, it seems more likely that the forces holding the molecule together operate only over distances something like the distance separating two neighbouring atoms in the ring, rather than over a distance comparable to the whole length of the molecule. In other words if these forces are a residuum of the atomic valence forces, we can hardly expect them to extend much beyond the limits of the individual atomic volumes. We therefore use for V the atomic volume of graphite, and calculate θ_m for benzene to be 159. From this and a table of values of the Debye function the values of the heat capacity of benzene due to the motions of the molecule have been computed, and are arranged in Table I, column 1.

In comparing these computed values, with the observed specific heat there is at high temperatures the difficulty that the observed heat capacity is due as much to the vibrations of the atom within the molecule as to the vibrations of the molecule as a whole; but as will be shown later, below 100°K., the purely atomic vibrations become negligible because of their higher frequencies so that we can compare the values calculated in the above manner with the observed heat capacity in this region of temperature. Figure 1 illustrates in the solid line (1) the computed total molal heat capacity for benzene. The circles represent the values observed by NERNST ²⁾. The agreement seems to justify the general line of argument.

There are also included here the values, computed in a similar manner, for hydroquinone together with the observed points ³⁾ as crosses. The broken lines show the heat capacities of the other organic substances

¹⁾ Physikal. Zeitschr. 11, 609, 1910. For the value of the empirical constant see NERNST, note 2, pag. 2.

²⁾ W. NERNST, Ann. d. Phys. 36, 395, 1911.

³⁾ LANGE, Z. Ph. Chem. 110, 351, 1924.

TABLE I.

The molal heat capacity of benzene. Melting point 278.6 °K.

T °K.	Vibrations				Expansion	Total Heat capacity		calc. —obs.
	Molecule Calories per degree	Carbon		Hydrogen		calc.	obs. ²⁾	
		⊥ to ringplane $\theta = 568$ ¹⁾	// to ringplane					
	I.	II.	III.	IV.	V.			
10	0.2					0.2	.3	—.1
20	1.7					1.7	1.7	0
30	4.0				0.0	4.0	4.5	—.5
40	6.1				0.1	6.2	6.6	—.4
50	7.5	0.0			0.2	7.7	8.0	—.3
60	8.7	0.1			0.4	9.2	9.4	—.2
80	9.9	0.5			0.7	11.1	11.1	0
100	10.5	1.3			0.9	12.7	12.9	—.2
120	11.0	2.4	0.0		1.1	14.5	14.4	+ .1
140	11.2	3.5	0.1		1.4	16.2	16.0	+ .2
160	11.4	4.6	0.2		1.6	17.8	17.4	+ .4
180	11.5	5.6	0.5		1.8	19.4	19.0	+ .4
200	11.6	6.4	0.9	0.0	2.1	21.0	20.5	+ .5
220	11.6	7.1	1.3	0.1	2.3	22.4	22.7	—.3
240	11.7	7.6	1.9	0.3	2.5	24.0	24.8	—.8
260	11.7	8.1	2.7	0.5	2.7	25.7	27.0	—1.3

observed by various authors in this region. It is interesting to note that the more compact molecules all have heat capacities in the neighbourhood of 12 calories per degree at 100°K. These substances follow a kind of DULONG and PETIT's law since at this temperature the molal heat capacity, which is principally due to the energy of molecular motion, approaches the equipartition value, it being 12 calories per degree instead of six, because of rotational motion. With additional degrees of freedom

1) Term II for $\theta = 511$, from ELLIS's general equation for C—C.

T = 60 80 100 120 140 160 180 200 220 240 260.

Term II = 0.2 0.8 1.9 3.1 4.3 5.4 6.3 7.1 7.7 8.2 8.7.

2) Note 2, page 746.

of low frequency, such as in heavy side chains, nitrobenzoic acid, or a long straight chain, butylalcohol, the values run somewhat higher as is to be expected.

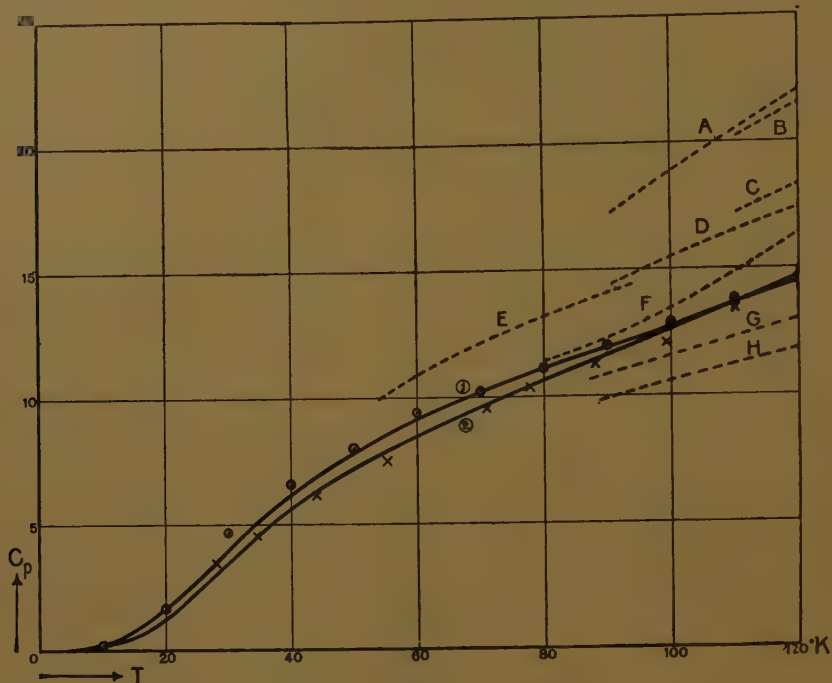


Fig. 1.

The molal heat capacity for Benzene (1) calculated, o observed ¹⁾;

Hydroquinone (2) calculated, \times observed ²⁾.

Dotted lines show observed heat capacity for: (A) Dextrose ³⁾, (B) Nitrobenzoic acid ⁴⁾, (C) Nitroaniline ⁴⁾, (D) Butylalcohol ⁵⁾, (E) Quinone ²⁾, (F) Glycerol ⁶⁾, (G) Ethylalcohol ⁵⁾, (H) Methylalcohol ⁵⁾.

§ 3. Turning next to the vibrations of the *individual atoms* within the molecule, the most promising source of information about frequency is the absorption spectra. While the molecular frequencies just discussed correspond to radiation frequencies (wave length of ca. $100\ \mu$) too far in the infra red to be studied at present, the evidence from the temperature of decomposition and other sources indicates that the radiation corresponding to the atomic frequencies should lie in the well known region of wave length below $15\ \mu$. Here there are several observations of the spectrum of benzene. First, in an extensive study of the vapour, HENRI ⁷⁾

¹⁾ W. NERNST, Ann. d. Phys. **36**, 395, 1911.

²⁾ FRITZ LANGE, Z. Ph. Chem. **110**, 351, 1924. Quinone given to 22°K .

³⁾ SIMON, Ann. Physik. (4) **68**, 241, 1922.

⁴⁾ D. H. ANDREWS, Journ. Am. Chem. Soc. **48**, 1293, 1926.

⁵⁾ PARKS, Jour. Am. Chem. Soc. **47**, 338, 1925.

⁶⁾ GIBSON and GIAUQUE, Jour. Am. Chem. Soc. **45**, 93, 1923.

⁷⁾ V. HENRI, Structure des Molecules, Paris 1925 p. 111.

has found the ultra violet spectrum to be well represented by the equation:

$$\frac{1}{\lambda} = 38612.4 + n 921.7 - p 162 + q 121.$$

The fundamental frequencies in the three variable terms, converted to the θ scale, are 1312, 230 and 172 respectively.

In the infra red region the absorption spectra of liquid benzene and related compounds have been studied by a number of investigators ¹⁾. Among the bands observed MARTON and ELLIS find considerable evidence for the existence of two series of bands. One of these, with fundamental frequency $\theta = 2226$, ELLIS ascribes to vibrations involving the C—H bond and it will be discussed later. The other series he considers as due to the C—C bond. Although the position of the series shifts somewhat among the different compounds considered, the wave lengths are fairly well represented by the equation:

$$\lambda_n = 28.0/n \quad n = 1, 2, 3, 4 \text{ etc.}$$

The evidence for this series in benzene is as follows. The band corresponding to $n = 1$, lies too far in the infra red to be observed, and the second harmonic, $n = 2$, is in the region at the limit of observation which in the case of benzene is uncertain. The band corresponding to $n = 3$ should lie at 9.35μ . According to the observations of BELL (loc. cit.) there is, in this case, no band at 9.35μ but two very prominent bands one at 8.4μ and one at 9.75μ . To secure the correct interpretation of these bands further evidence is undoubtedly necessary, but as a tentative hypothesis in order to secure frequency values for calculating the specific heat, we make the following assumptions. The band at 8.4μ is considered to be the band for $n = 3$ in the ELLIS C—C series which, for the case of benzene, is taken as having a fundamental frequency corresponding to 25.2μ instead of 28μ which was the average for a number of compounds. This value gives an equation

$$\lambda_n = 25.2 \mu/n$$

which seems to fit the bands for $n = 4, 5, 6$ etc. nearly as well as ELLIS's general equation. Moreover it is not unreasonable to suppose that the fundamental frequency for C in benzene is somewhat higher than for most organic compounds because the interatomic forces in the benzene ring are generally regarded as comparatively strong. The fundamental frequency on the θ scale for this series is 568.

As a second assumption the band at 9.75μ is identified with the funda-

¹⁾ W. W. COBLENTZ, Investigations of Infra Red Spectra, Carnegie Inst. Publ. Washington D. C. 1906.

J. W. ELLIS, Phys. Rev. 23, 48, 1924; 27, 298, 1926 contains a summary of the previous work in this field.

L. MARTON, Z. Phys. Chem. 117, 97—128, 1925.

F. K. BELL, Journ. Am. Chem. Soc. 47, 2811, 1925.

mental frequency in HENRI's equation, $\theta = 1312$, which would correspond to a band at 10.9μ . The shift toward higher frequency is regarded as due to the closer packing in the liquid state as compared with the vapour. This means that bands should be found in accordance with the equation

$$\lambda_n = 9.75 \mu/n \quad n = 1, 2, 3, \dots \text{etc.}$$

Unfortunately these bands coincide with other deep bands so that it is difficult to prove the existence of this series, but such a series is not unreasonable. The fundamental frequency in the θ scale for this series is 1470.

In order to account for these bands in terms of atomic vibrations we regard the carbon atom as having only two fundamental frequencies. The higher corresponds to vibrations, with large restoring force, in a direction *along* the carbon to carbon bonds, that is, *in* the plane of the benzene ring. It has the value $\theta = 1312$ (HENRI) in the vapour state and $\theta = 1470$ in the liquid. The second fundamental frequency corresponds to vibration *not* along any C—C bonds but perpendicular them, that is, perpendicular to the plane of the benzene ring. This vibration, with a much smaller restoring force, has the frequency $\theta = 230$ in the gas, and $\theta = 568$ in the liquid. The increase of the value in passing from the gas to the liquid state is again ascribed to packing and is so much larger than in the previous case because the vibration is perpendicular to the ring and more retarded by the presence of neighbouring rings in the liquid state.

The correctness of identifying these frequencies with the vibration of the carbon atoms is supported by the "melting point", i. e. temperature of decomposition for the benzene ring, calculated from LINDEMANN's melting point-frequency formula, employing these values of the frequency. For $\theta = 568$ the temperature of decomposition is about 800°K ., certainly of the right order of magnitude.

This picture lends itself most readily, of course, to the centric formula for benzene, especially that recently proposed by PAULING ¹⁾. Adopting this view, each carbon atom is assigned one degree of freedom perpendicular to the plane of the ring with frequency $\theta = 568$ and two in the plane, with frequency $\theta = 1470$. The two terms in the specific heat equation for the heat capacity of the carbon atoms are thus ²⁾

$$6 R F_E \left(\frac{568}{T} \right) + 12 R F_E \left(\frac{1470}{T} \right).$$

This assumes that the frequencies are not greatly changed in passing from the liquid to the solid state.

There now remain only the vibrations of the hydrogen to be accounted

¹⁾ LINUS PAULING, Jour. Am. Chem. Soc. **48**, 1132, 1926.

²⁾ The values of these terms are given in columns II and III of table I. In the supplement to table I are given the values for term II calculated with $\theta = 511$, secured from Ellis's general C—C equation, $\lambda = 28.0 \mu/n$. The differences between the two sets of values for Term II are no greater than the uncertainties in the theory.

TABLE II.

The molal heat capacity of hydroquinone $C_6H_4(OH)_2$, melting point 445.1° K.

T° K.	Vibrations				Expansion V.	Total Heat capacity		calc.-obs.
	Molecule calories per degree I.	Carbon and oxygen		Hydrogen IV.		calc.	obs.	
		⊥ to bonds II.	// to bonds III.					
	$6 RF_D \left(\frac{170}{T} \right)$	$8 RF_E \left(\frac{568}{T} \right)$	$16 RF_E \left(\frac{1470}{T} \right)$	$18 RF_E \left(\frac{2226}{T} \right)$	$(C_v)_{mol.}^2 \frac{T \times 0.214}{445.1}$			
10	.2					.2		
20	1.4					1.4	1.8	-.4
30	3.5				0	3.5	3.8	-.3
40	5.6				.1	5.1	5.4	+.3
50	7.1	0.0			.1	7.2	6.9	+.3
60	8.2	0.1			.2	8.5	8.3	+.2
80	9.6	0.7			.4	10.7	10.4	+.3
100	10.4	1.7			.5	12.6	12.1	+.5
120	10.8	3.2	0.0		.7	14.7	13.9	+.6
140	11.1	4.7	.1		.8	16.7	15.8	+.9
160	11.3	6.2	.3		1.0	18.8	17.7	+1.1
180	11.5	7.4	.7		1.1	20.7	19.7	+1.0
200	11.5	8.5	1.1	0	1.3	22.4	21.8	+.6
220	11.6	9.4	1.8	.1	1.4	24.3	23.9	+.4
240	11.6	10.2	2.6	.3	1.6	26.3	26.0	+.3
260	11.7	10.8	3.6	.5	1.7	28.3	28.1	+.2
280	11.7	11.4	4.7	.9	1.9	30.6	30.2	+.4
300	11.8	11.9	5.8	1.2	2.0	32.7	32.4	+.3
320	11.8	12.3	7.0	1.6	2.1	34.8	34.5	+.3
340	11.8	12.7	8.1	2.2	2.3	37.1	36.6	+.5
360	11.8	13.0	9.2	2.8	2.4	39.2	38.7	+.5
380	11.8	13.3	10.4	3.5	2.6	41.6	40.8	+.8
400	11.8	13.5	11.5	4.2	2.7	43.7	42.9	+.8
420	11.9	13.7	12.6	5.0	2.8	46.0	45.0	+1.0
440	11.9	13.8	13.5	5.9	3.0	48.1	47.2	+.9

$$+ 18 RF_E \left(\frac{2226}{T} \right) + \left[6 RF_D \left(\frac{159}{T} \right) \right]^2 \frac{T}{278.6} \times 0.0214.$$

IV. HYDROGEN.

V. EXPANSION.

The values of these terms separately, the sum, and the observed values of the heat capacity are arranged in Table I. The agreement is somewhat better than would be expected in view of the complex structure of such a molecule. On the other hand it is not so surprising, in view of the possibility of resonance effects which may cut down the number of frequencies, and also in view of the simplicity of the observed spectrum in which all the prominent bands are accounted for even by this simple theory. As an extension of these ideas, formulas of similar nature have been developed for the other forty or so organic compounds for which the heat capacities have been measured up to the present time, and it is found that, with the frequencies employed for benzene, the heat capacities of these compounds in the solid state can be accounted for fairly satisfactorily. This seems to show that in most organic compounds the valence forces are roughly the same. As an example there is given in Table II the heat capacity terms and total for hydroquinone, para $C_6H_4(OH)_2$, which illustrates better than benzene the way the hydrogen vibrations and the carbon vibrations parallel to the ring plane contribute to the heat capacity at the higher temperatures.

The observed values are secured by interpolation from the following sources; LANGE ¹⁾, ANDREWS, LYNN and JOHNSTON ²⁾ and ANDREWS ³⁾.

The fact that this theory is in accord with the facts over such a wide range of temperature and for so many compounds seems to show that the vibrations are, generally speaking, of the types which have been outlined.

It is hoped that when further measurements of both specific heats and absorption spectra are made, a more comprehensive and detailed theory along these lines will result.

¹⁾ FRITZ LANGE, Z. ph. Chem. **110**, 351, 1924.

²⁾ ANDREWS, LYNN and JOHNSTON, Jour. Am. Chem. Soc. **48**, 1274, 1926.

³⁾ D. H. ANDREWS, Jour. Am. Chem. Soc. **48**, 1293, 1926.

